12: **Overview of nanomanufacturing processes: top-down vs. bottom-up**

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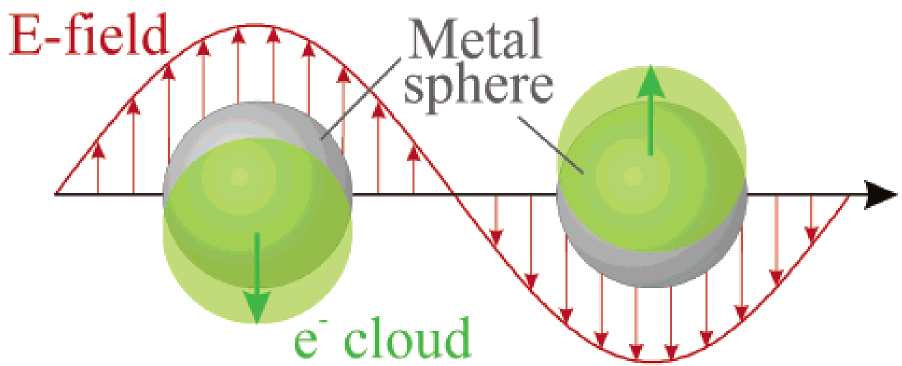
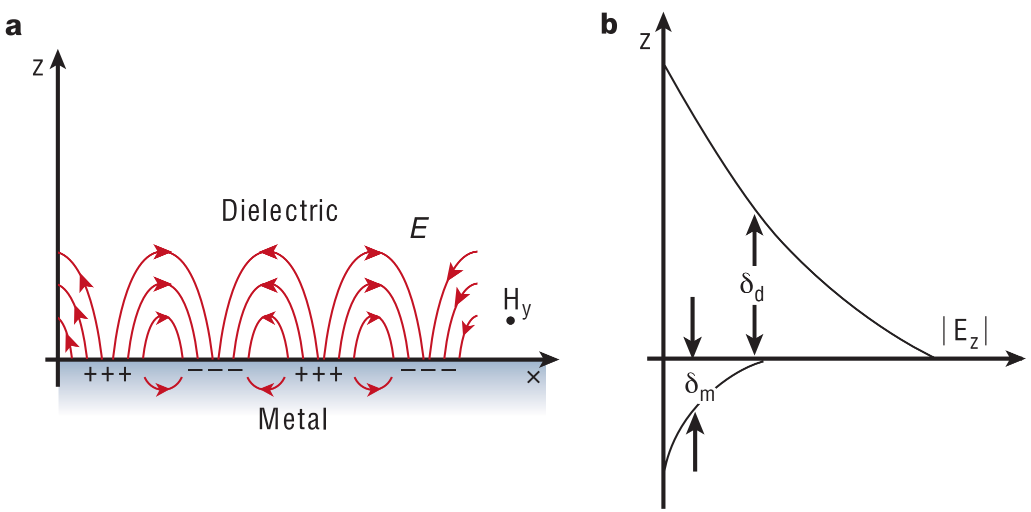
Announcements

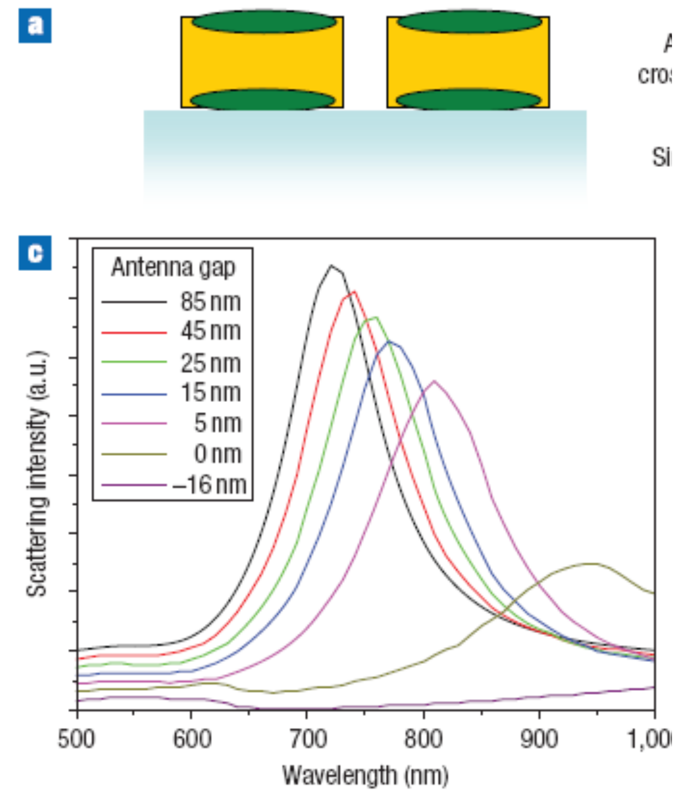
- I think everyone signed up for the video assignment
- See revised syllabus
  - Lectures, upcoming assignments and exam
- See project description
  - Compatibility/conflicts with your research
  - Overlap with other course projects
- PS3 to be posted by next Monday
- Expectations for exam(s)
  - Lecture content
  - HW assignments and concepts therein

Recap: surface plasmon resonance (SPR)

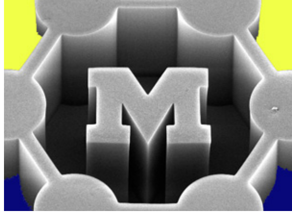
- Electromagnetic charge density waves; surface plasmon resonance (SPR) occurs when a resonance of the charge density wave matches the frequency of the driving field



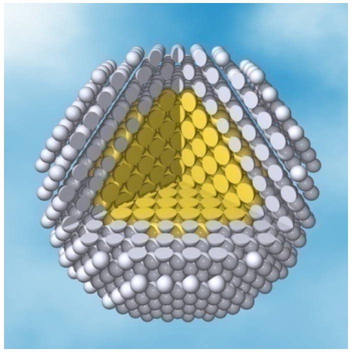




Course outline



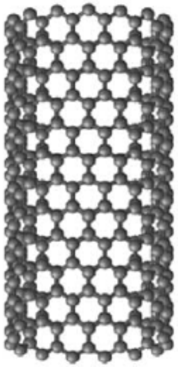
0: Introduction to nanotechnology



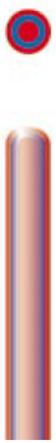
1: Properties of nanostructures ("building blocks")

2: Interactions among nanostructures

3: Synthesis of nanostructures



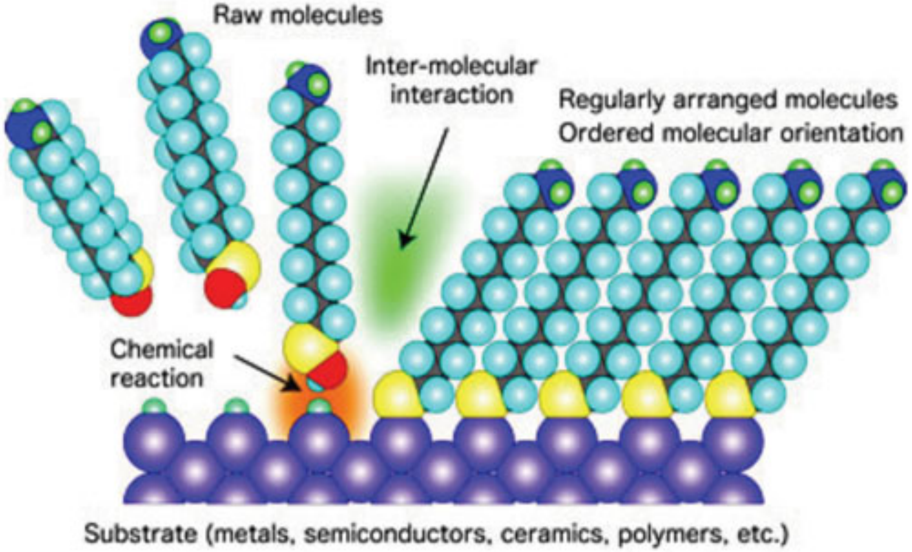
4: Assembly of nanostructures and property scaling



5: Case studies and project presentations

→ a **manufacturing** project

Nanomanufacturing: top-down vs. bottom-up



→In coming lectures, we will focus on bottom-up methods, and we will emphasize their *integration* with top-down methods

→Rigorously question the limitations of these methods for **true nanomanufacturing**

http://www.aist.go.jp/aist_e/aist_today/2007_23/nanotec/nanotec_02.html

Nanomanufacturing Process Needs

Fabrication Techniques

- Embedded Sensors
- Remote Manufacturing
- Automation
- Automation with Self-calibration and Adjustment

Modeling and Control

- Modeling and Simulation (M&S) Tools
- Automatic Comparison to M&S Data
- Accurate Modeling at nm scale

Economics
-Cost
- EHS
- High Throughput

Metrology

- International Standards
- Identification of New Measurement Parameters
- Calibration Tools Nano-characterization

Nanostructures into Devices / systems

- Interfaces to Micro and Macro
- Whole System Scale-up
- Rapid Characterization of 3D structures

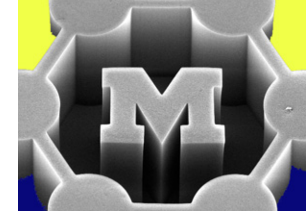
Today's readings

Nominal: (ctools)

- "Fabrication methods", excerpt from Introduction to Nanoscience

  → read as a survey

- DARPA TBN BAA, pages 1-10



DARPA tip-based nanofabrication (TBN)

- "The primary goal is to develop the capability to fabricate nanostructures, such as nanowires, nanotubes, and quantum dots with nanometer-scale control over the size, orientation, and position of each nanostructure. With this capability, real technologies based on nanowires, nanotubes, and quantum dots, as well as many other nano-scale structures, should be possible for the first time."

Metric	*Unit*	*Phase I*	*Phase II*	*Phase III*
Feature Position Control	nm	50	25	5
Feature Size Control (1)	% of dimension	10%	3%	1%
Heterogeneity (2)		2 values of one parameter	5 values of 2 parameters	Continuous control over 2 parameters
Feature Rate (3)		1/min Single tip	5/min/tip 5-tip array	60/min/tip 30-tip array
Tip Shape Variation (4)	% of dimension	Height<10%, Radius<20% 100 operations	Height<5%, Radius<10% 1000 operations	Height<1%, Radius<3% 1e6 operations
Tip Height Sensing	nm	20 nm	10 nm	2 nm

DARPA TBN program

- "For the purpose of this BAA, **controlled nanomanufacturing** is defined as automated, parallel fabrication of individual nanostructures with control over position, size, shape, and orientation at the nanometer scale, including the ability to fabricate devices with controlled differences in size, shape, and orientation at different positions. This capability should include the ability for in-situ detection of the nanostructure position, size, shape, and orientation, and the ability to repair or re-manufacture structures as needed."

DARPA TBN program

- "Presently, controlled nanomanufacturing is not possible. There have been numerous demonstrations of the capability to grow, deposit, or manipulate nanostructures in recent years, but these all suffer from significant deficiencies when viewed against the above stated goal.
  - For example, dense, aligned "forests" of carbon nanotubes can be grown, even with pre-growth lithography to define the regions of growth. This technique, however, cannot controllably grow individual nanotubes, or control their orientation or dimensions.
  - There are examples of quantum dot growth from catalyst seeds with the potential to create large arrays with high uniformity. There is no ability, however, for controlled manufacturing of patterned arrays of 2 different quantum dots, and there is no ability to repair the nonuniformity that typically arises from these growth processes.
  - There are examples of methods for capturing, manipulating, and placing individual nanowires into arrangements needed for device construction, but these are very slow, rely on a nearby "cache" of suitable sizes and shapes, and very challenging methods for manipulation, metrology and repair.
  - None of the presently-emerging approaches appear to provide a path to controlled nanomanufacturing."

DARPA tip-based nanofabrication (TBN)

Metric	*Unit*	*Phase I*	*Phase II*	*Phase III*
Feature Position Control	nm	50	25	5
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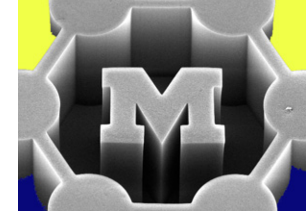
Tip Height Sensing	nm	20 nm	10 nm	2 nm

- What are our current capabilities?

DARPA TBN program

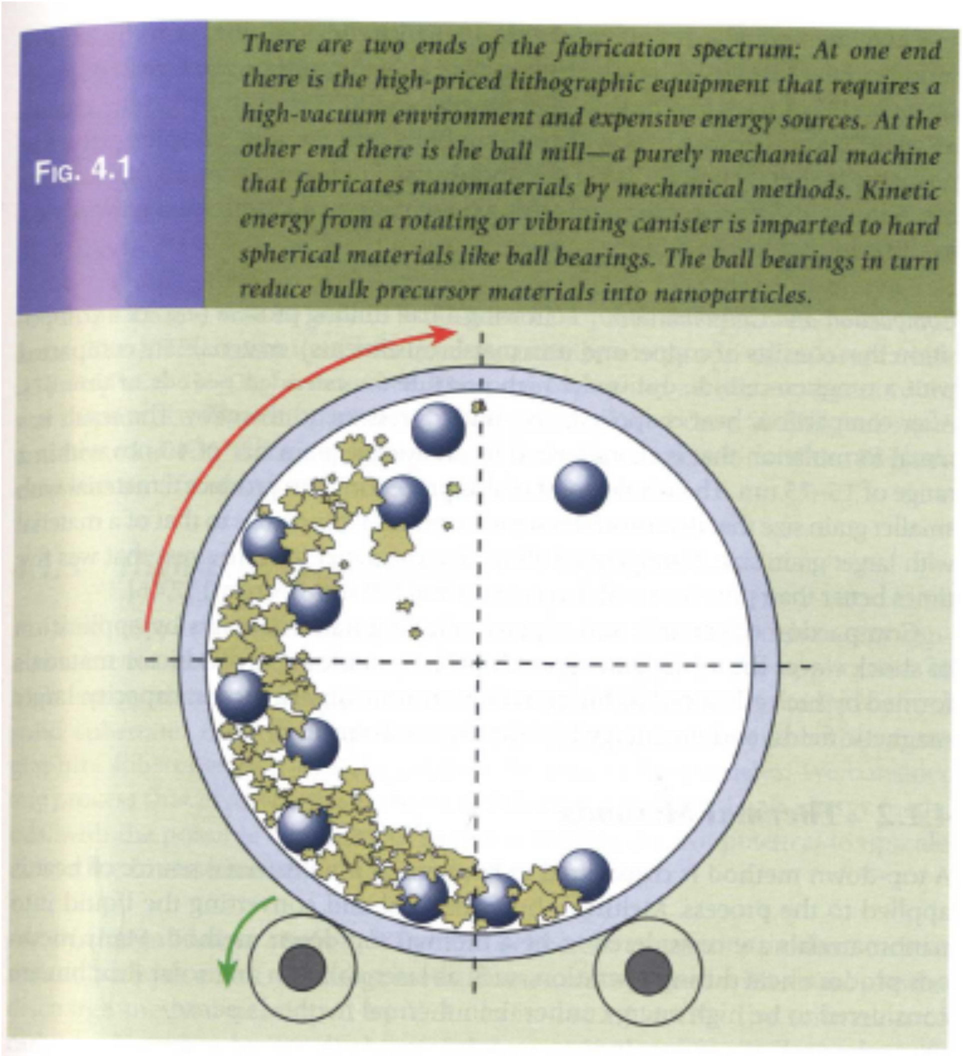
- "…additional features that provide interesting or unexpected advantages in controlled nanomanufacturing
  - provide structure-by-structure control over other characteristics of nanostructures. For example, the chirality of carbon nanotubes…
  - the ability to fabricate structures with controlled variations in other properties, such as conductivity, crystallinity, crystal orientation…
  - methods that require minimal preparation of the substrate; and, approaches which can be carried out on ordinary widely available substrates are preferred over approaches that require unusual materials, crystal orientations, or complicated topographies.
  - approaches which are compatible with the presence of pre-existing structures or devices, such as foundry CMOS.
  - approaches that can minimize the separation between preexisting CMOS and nanomanufactured structures, and is especially interested in approaches that can build interconnects between CMOS and nanostructures.

“Top-down” methods

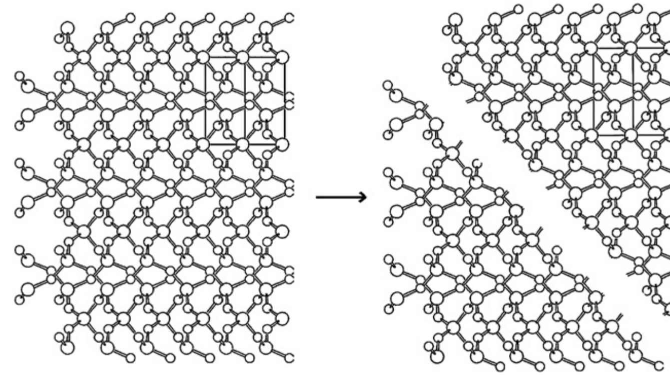


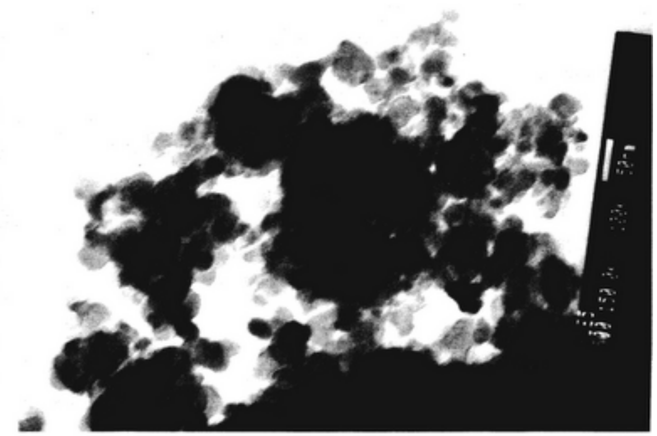
- Begin with bulk materials (top) that are subsequently reduced into nanostructures (down) by way of physical, chemical, or mechanical processes.
- Examples
  - Mechanical
    - Milling
    - Extrusion
    - Grinding
  - Thermal/chemical/high-energy
    - Evaporation, sputtering, ablation
    - Reactive/chemical etching
    - Combustion
    - Sonication
  - Patterning methods
    - Optical and physical lithography
    - Tip-based fabrication

The simplest: ball milling



Si





Transmission electron micrograph for 5 hours dry milled zinc ferrite.

- There are many “different” energetics at work here: deformation, bond-breaking, thermal

Arc discharge production of CNTs

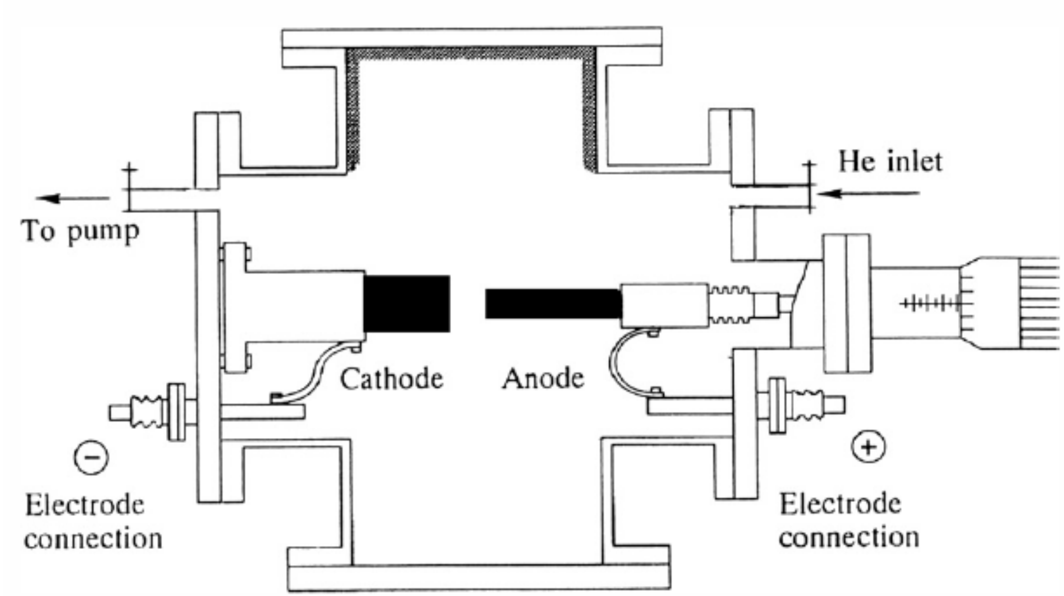
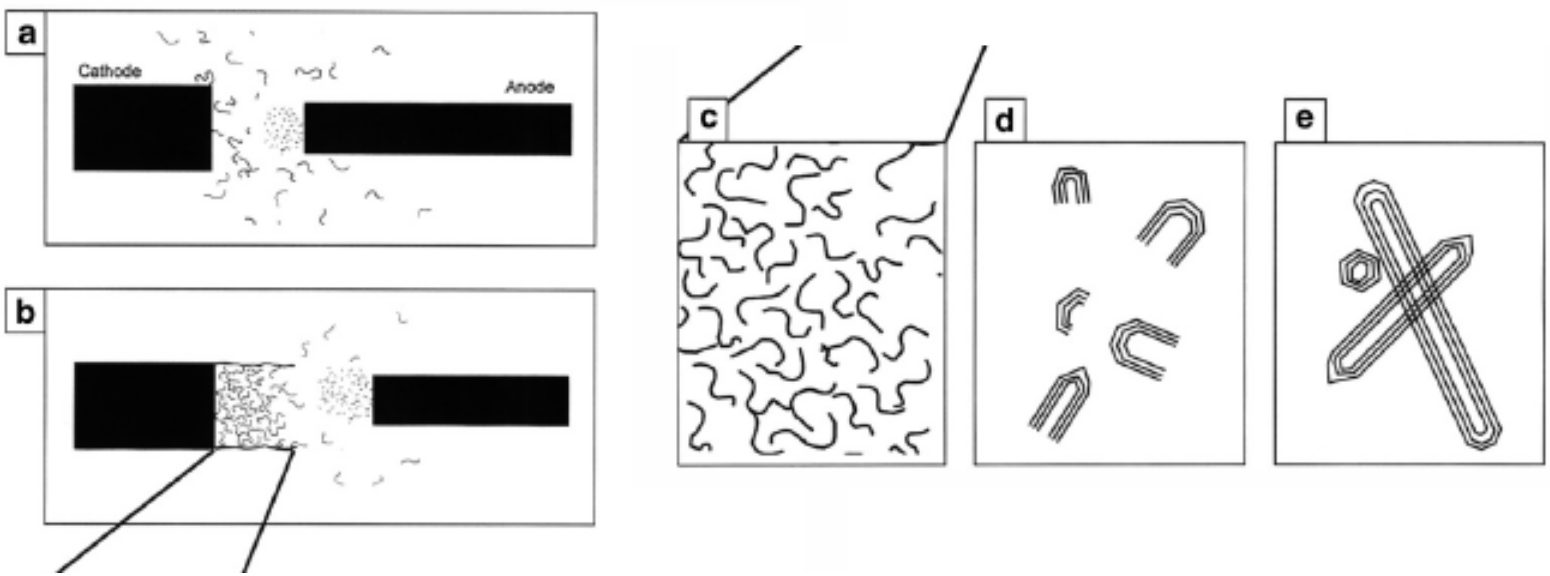


Fig. 1. Diagram of typical arc-evaporation apparatus for the production of nanotubes.



Harris, *Carbon* 45:228, 2007.

Laser ablation production of CNTs

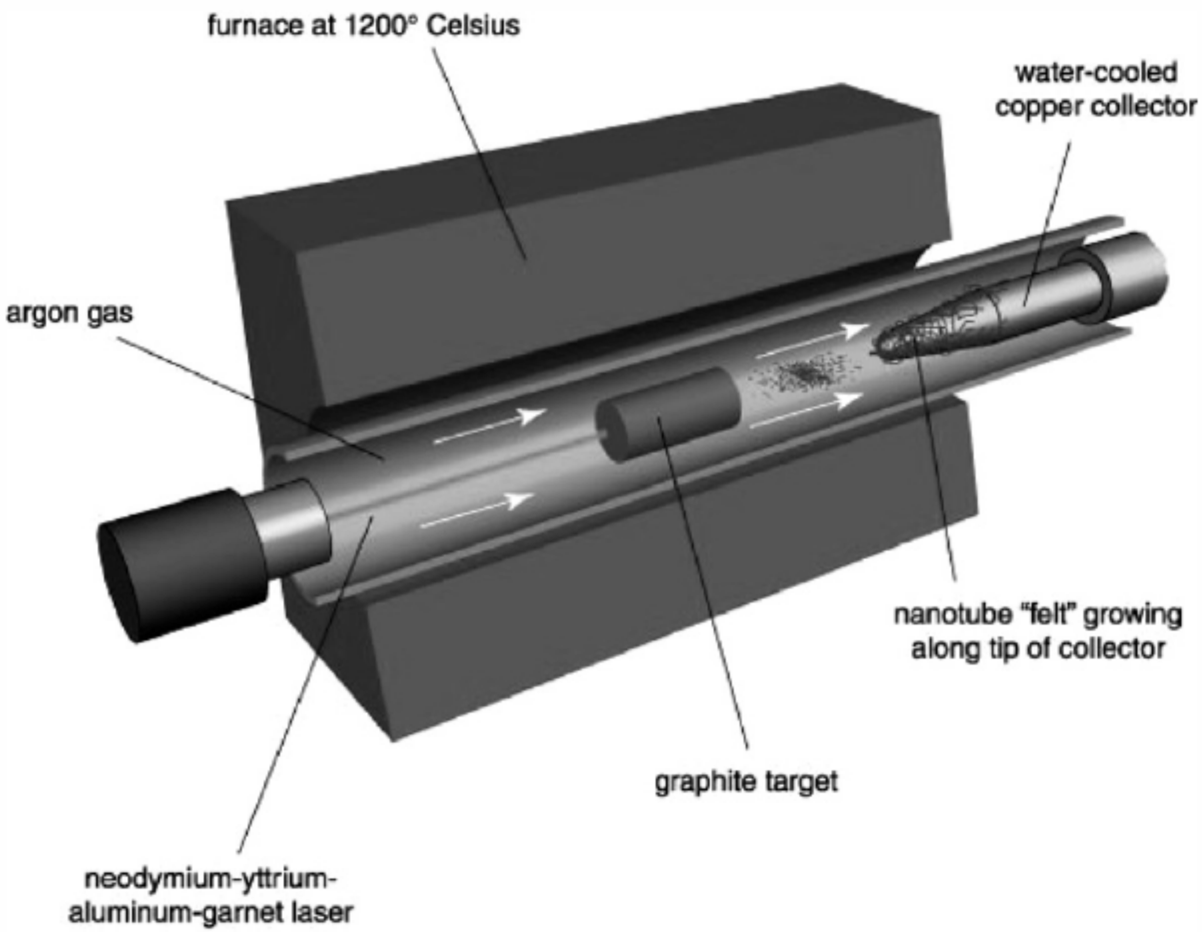
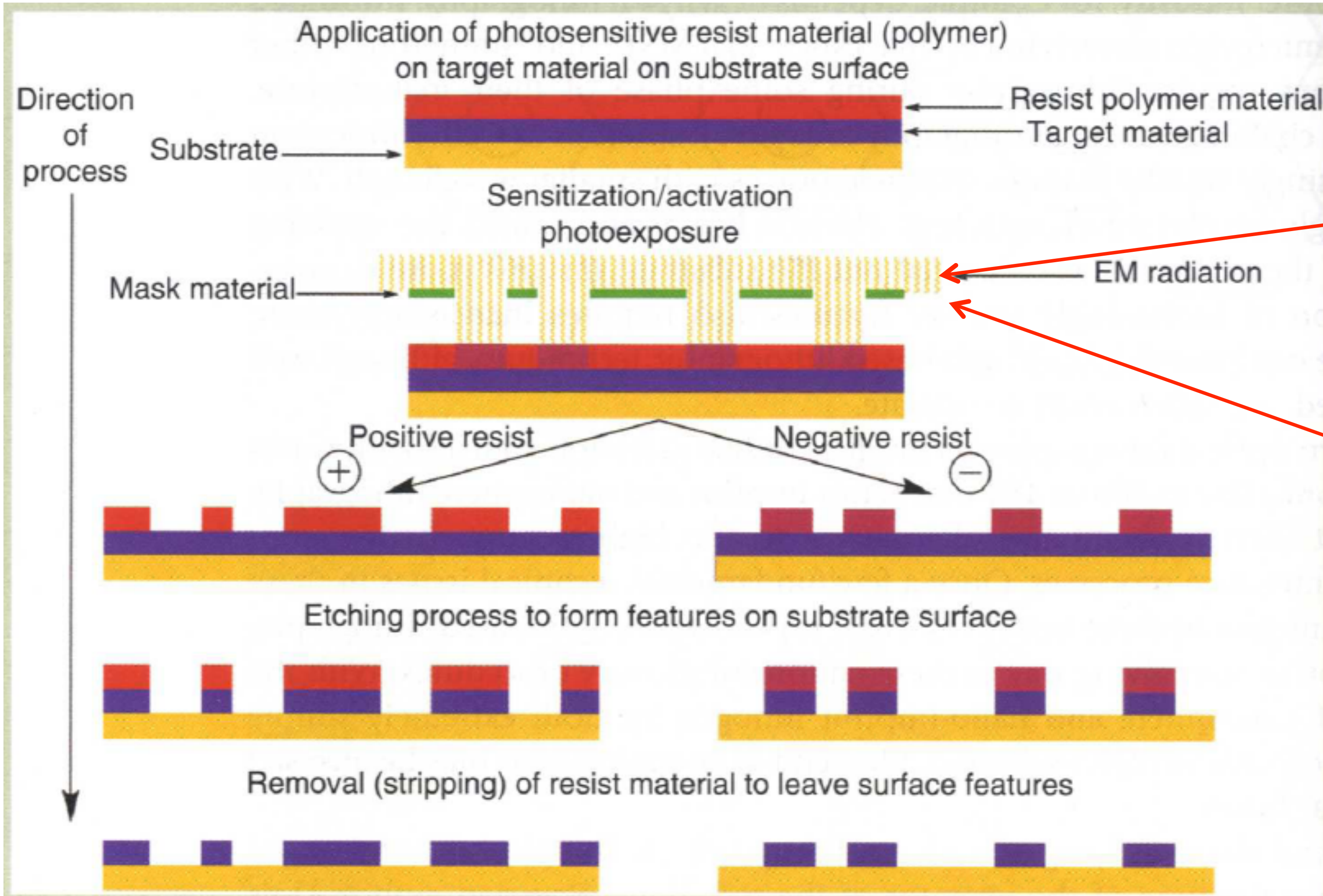


Fig. 5. Oven laser-vaporisation apparatus for the synthesis of single-walled carbon nanotubes [39].

Harris, *Carbon* 45:228, 2007.

Lithography

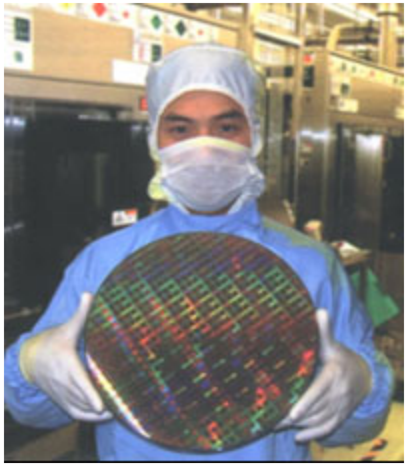


Type of radiation

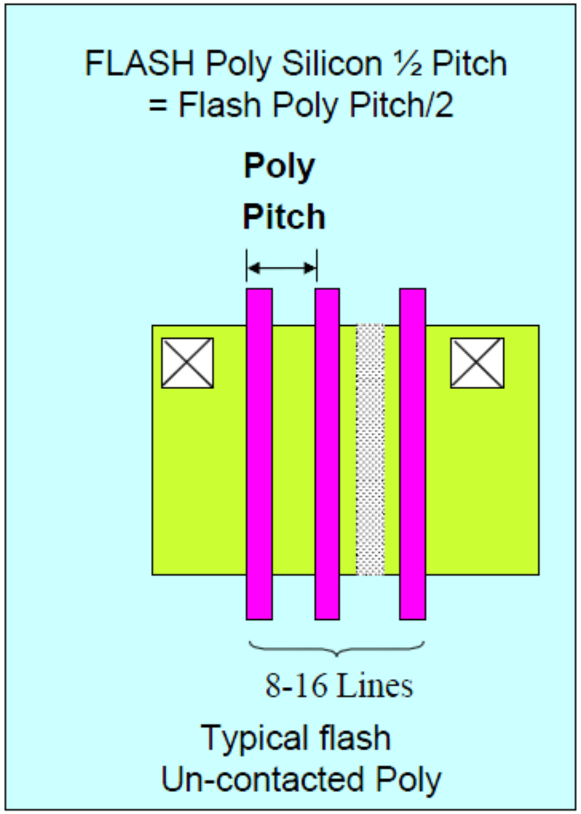
(light, UV, X-ray, e-beam)

Mask vs. direct write (serial vs. parallel)

Hornyak, Dutta, Tippals, Rao. Introduction to Nanoscience

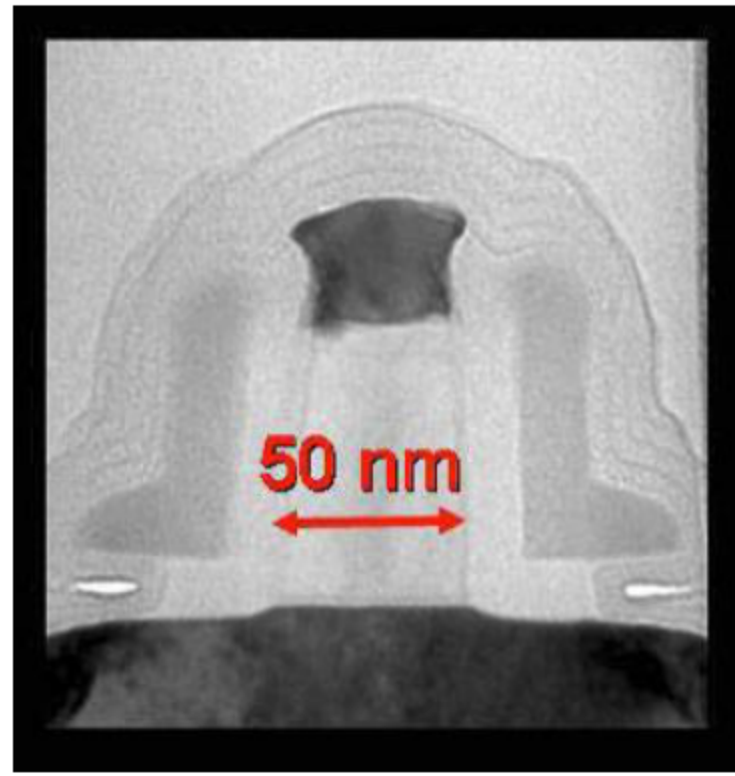


(silicon wafer)



Source: 2009 ITRS - Exec. Summary Fig 1

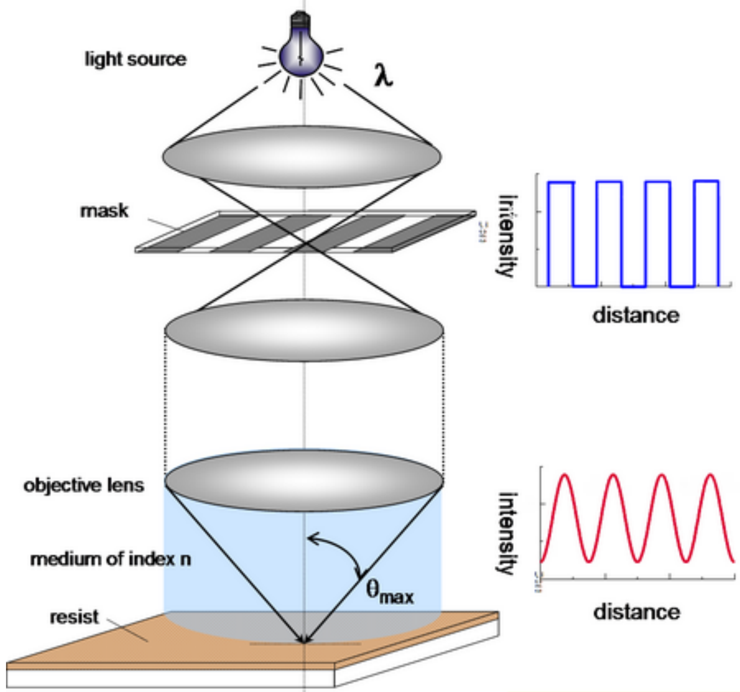
Work in Progres



“65 nm” technology

Immersion lithography

- Enhance resolution by placing a liquid medium between lens and sample
  - Liquid has a high refractive index.
  - Must have low absorption at the chosen wavelength (e.g., 193 nm).
  - Must be compatible with lens and photoresist, and not contaminate.



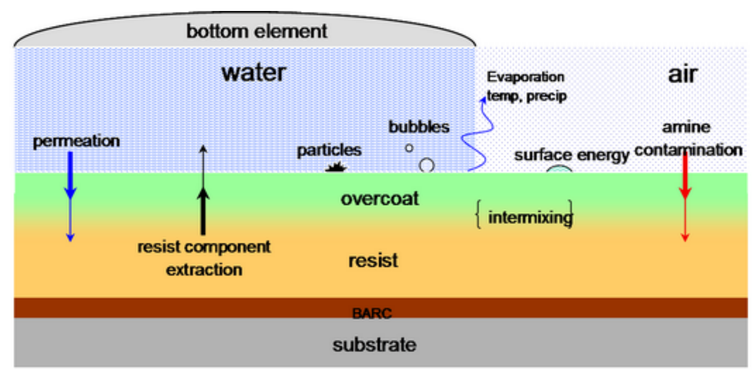
$$NA = n \times \sin(\theta_{max})$$

Schematic diagram of the optics of a projection exposure lithography system

$$W_{\min} = \frac{k\lambda}{NA}$$

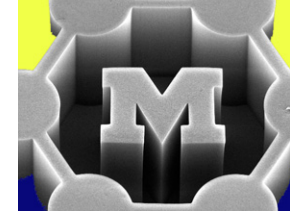
Constant (<1) X wavelength ($k\lambda$)

Numerical aperture (> 1) or refractive index (NA)

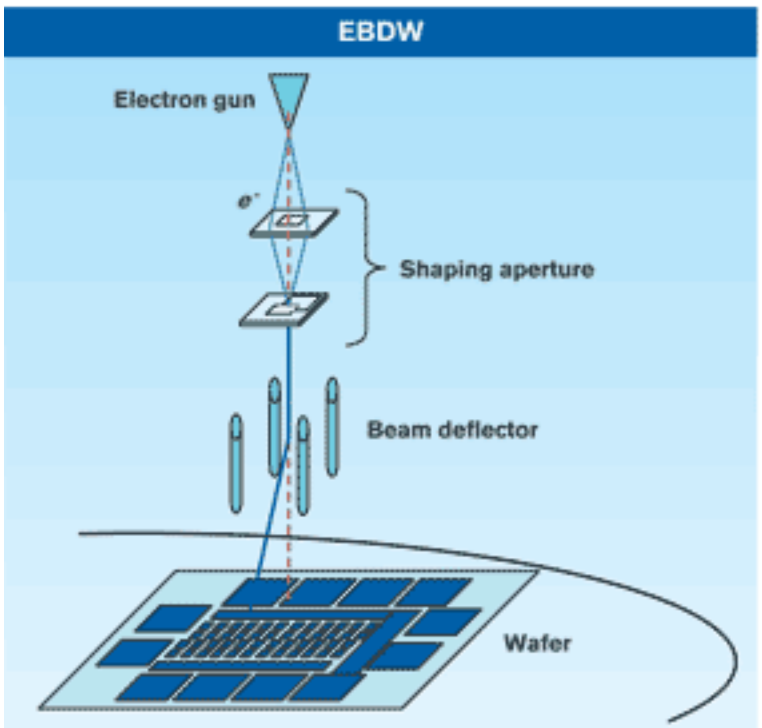


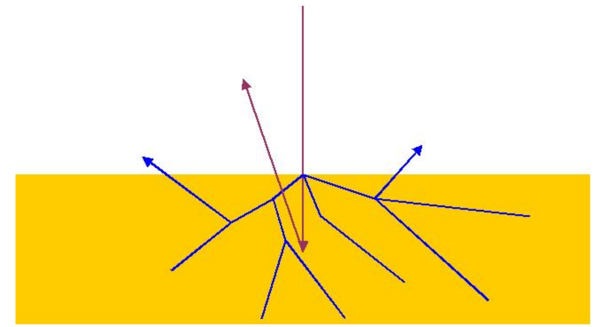
Schematic showing factors of concern at resist/overcoat/fluid interfaces

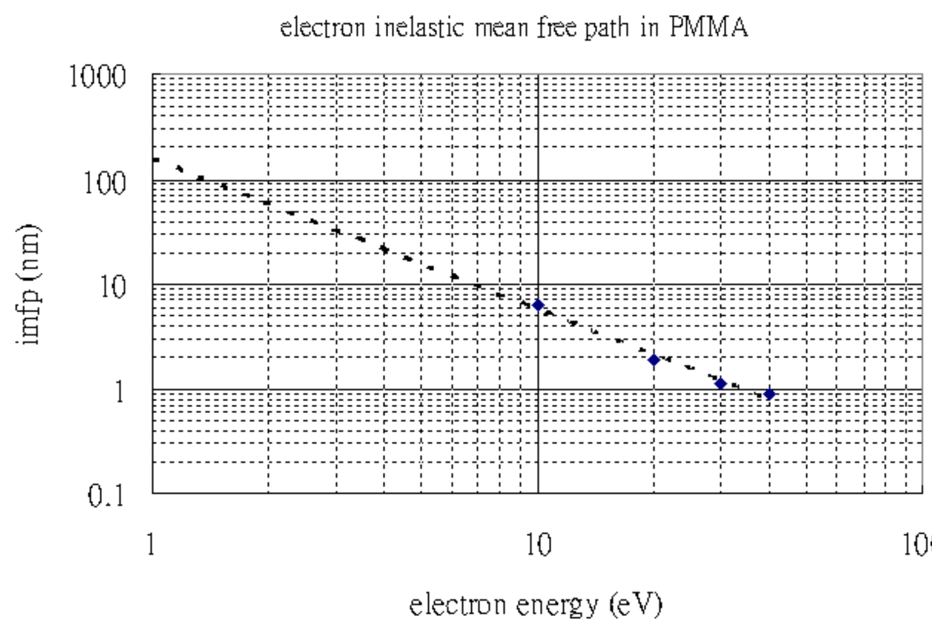
E-beam lithography



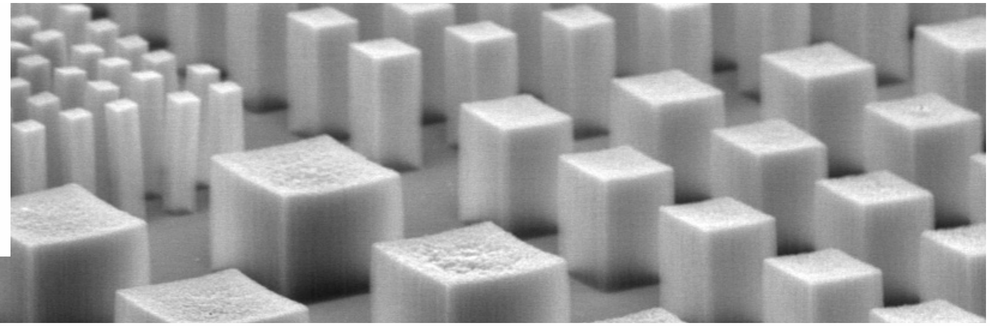
- Use an electron beam instead of light
- Practical resolution limited by electron scattering of the photoresist; linewidths <20 nm and energies 10-50 kV
- Inherently a serial process (slow); maskless







CNT microstructures vs. individual CNTs



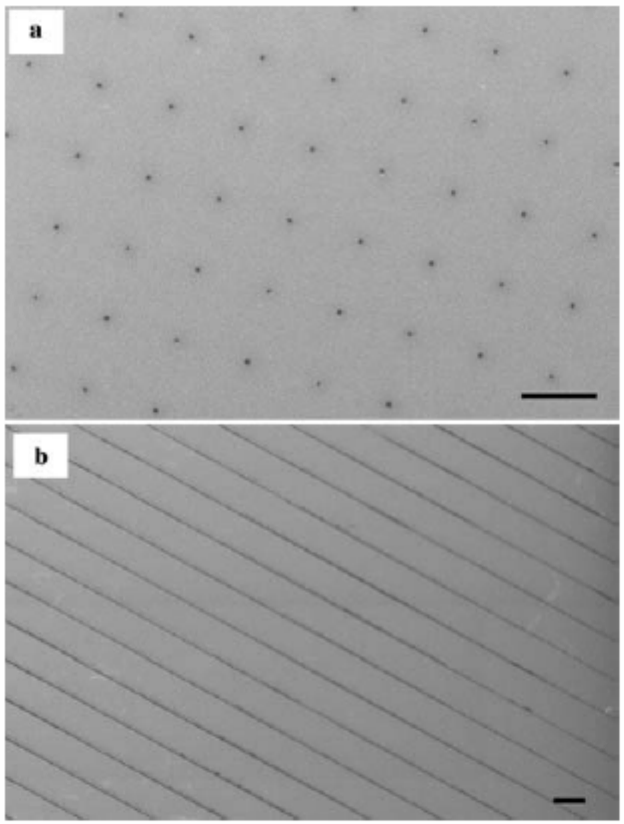


FIGURE 11 SEM images of as-printed Co colloid (a) *dot* and (b) *line patterns* (scalebars 4 μm, 3 μm, respectively)

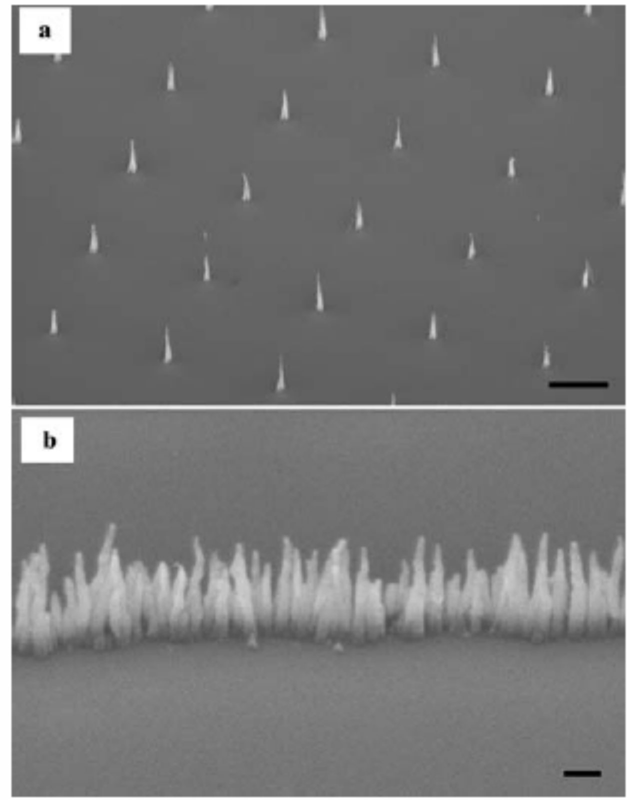
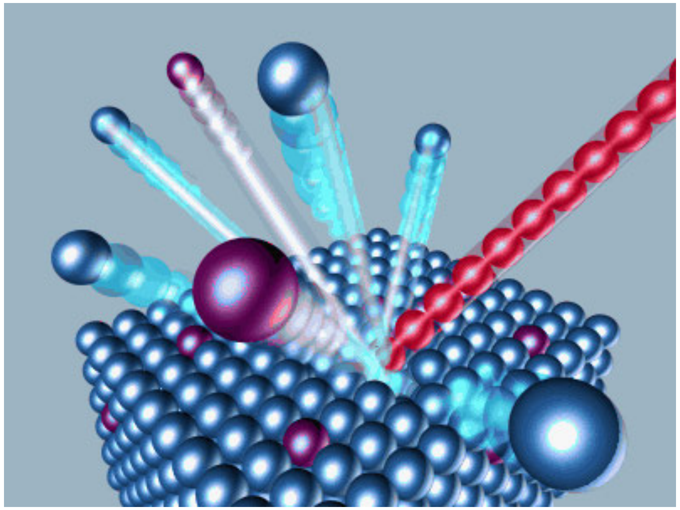


FIGURE 12 SEM images of (a) *dot* and (b) *line patterned*, aligned CNF arrays. Growth conditions: 1 : 4 C_2H_2 : NH_3 flow at 600 V DC bias, 500 °C for 15 min (scalebars 2 μm, 100 nm, respectively)

Hofmann et al., *Appl. Phys. A* 81:1559, 2005.

Focused ion beam (FIB) milling



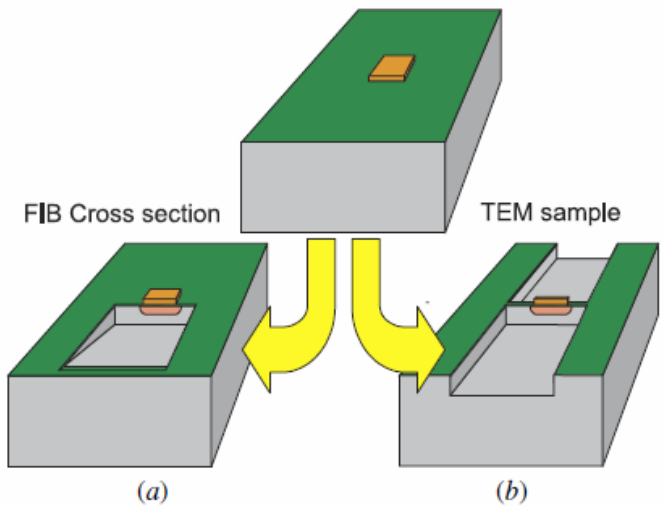
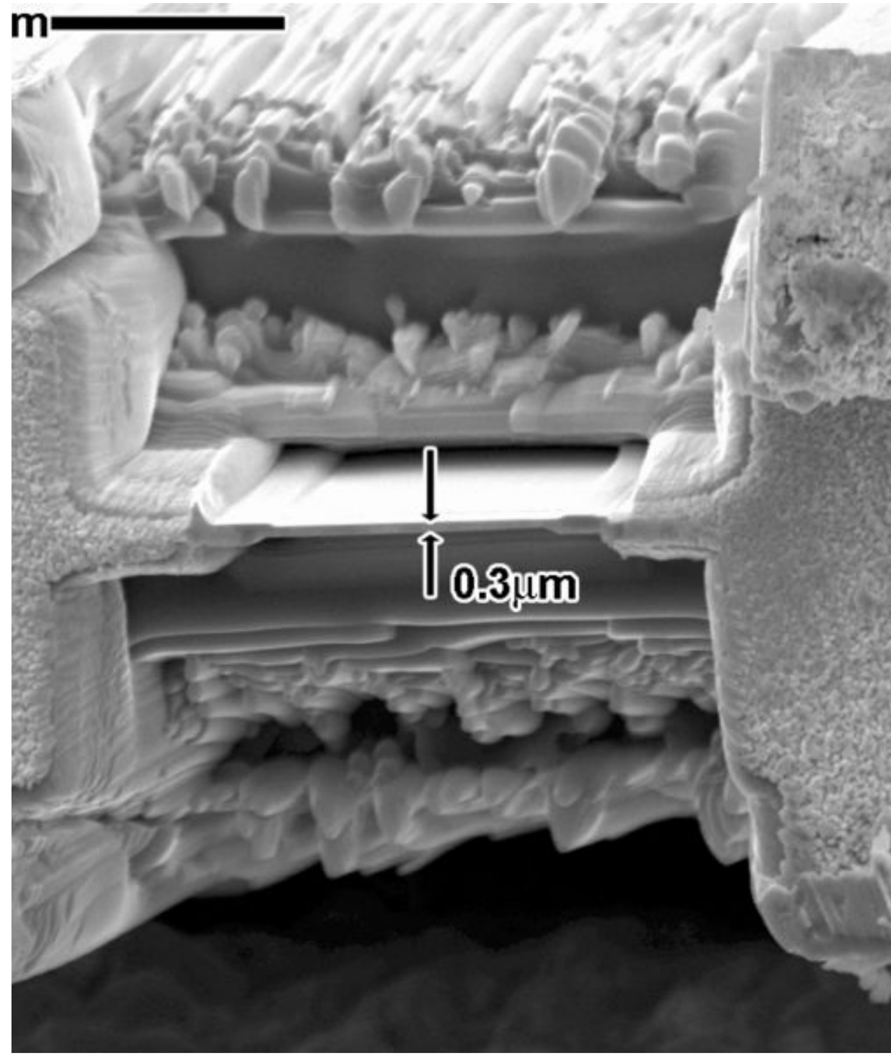


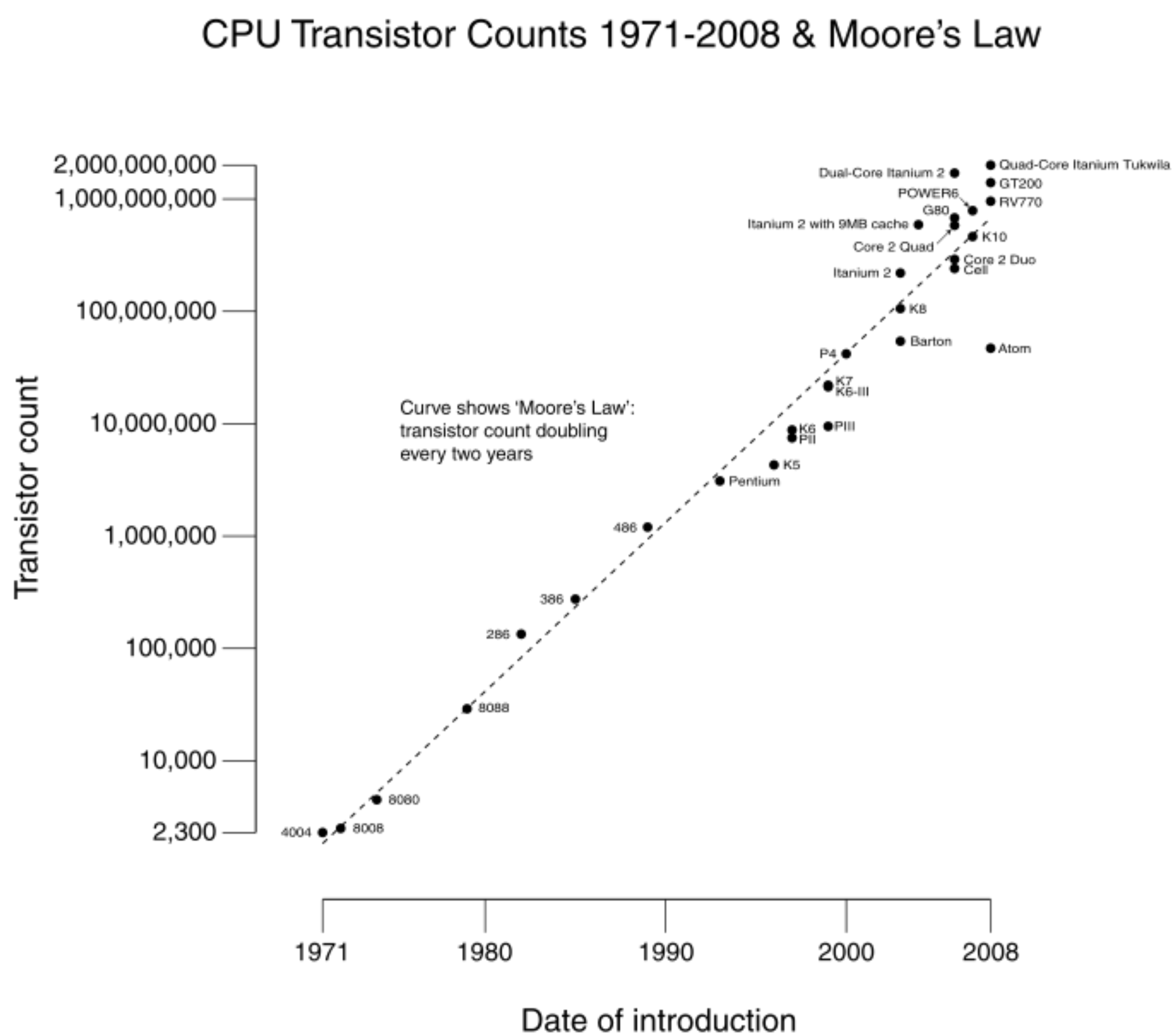
Figure 9. Sample with feature of interest can be (*a*) cross sectioned in the FIB. The section can be advanced until desired feature appears or (*b*) it can be prepared for inspection in a TEM.



http://commons.wikimedia.org/wiki/Image:Fib_tem_sample.jpg

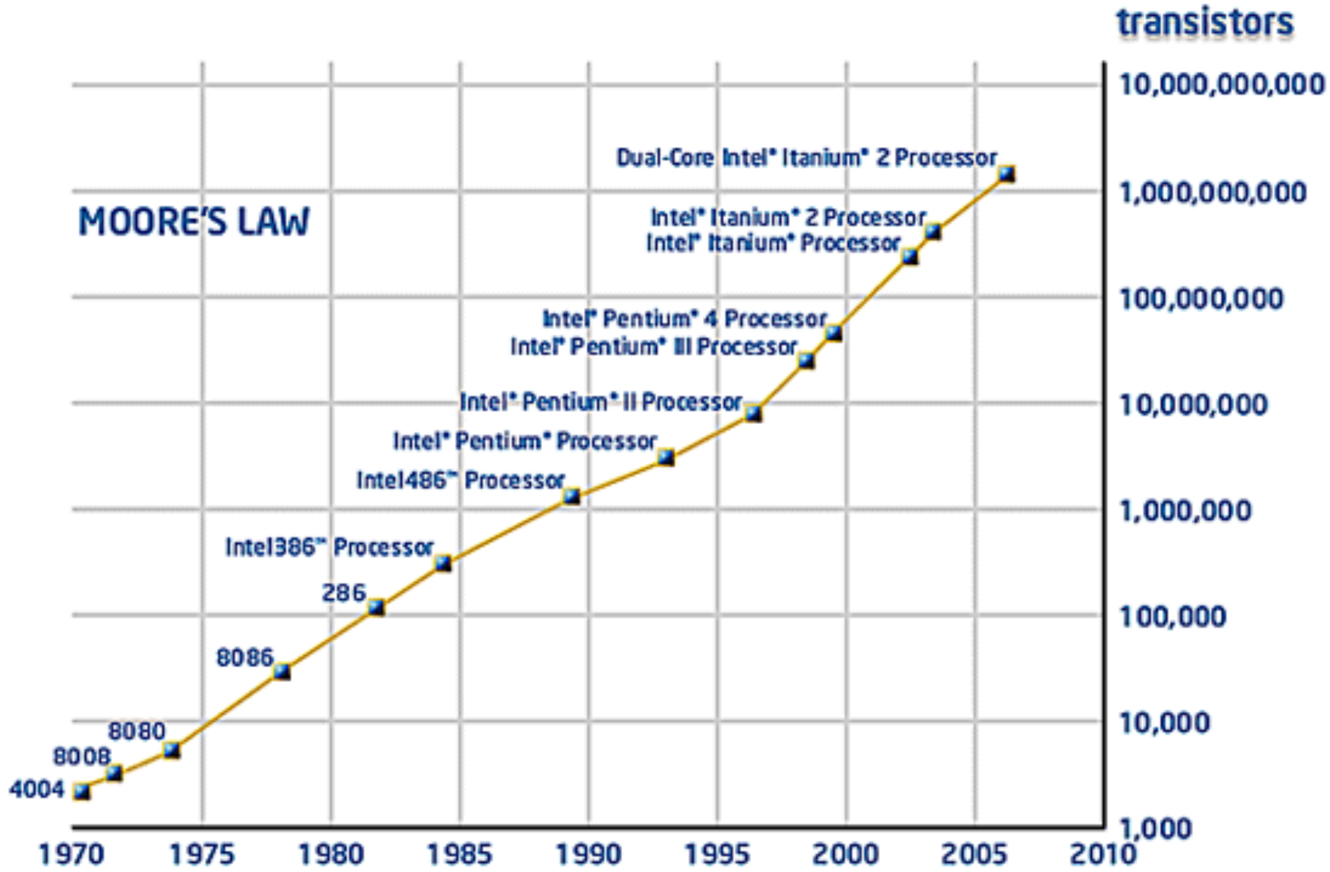
Reyntjens and Puers, J. Micromechanics and Microengineering, 11:287-300, 2001.

Moore's law

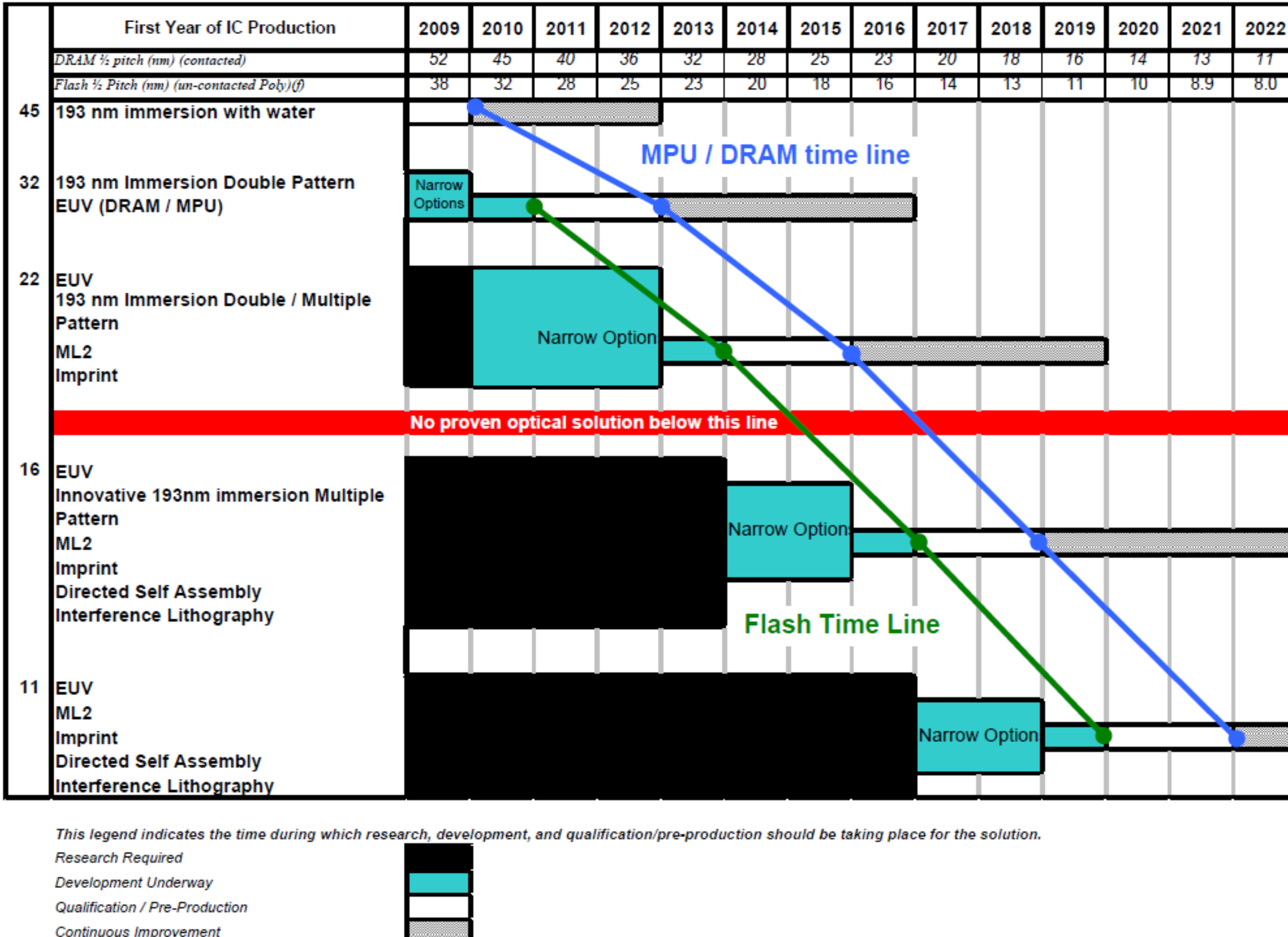


http://en.wikipedia.org/wiki/Moore's_law

Moore’s law

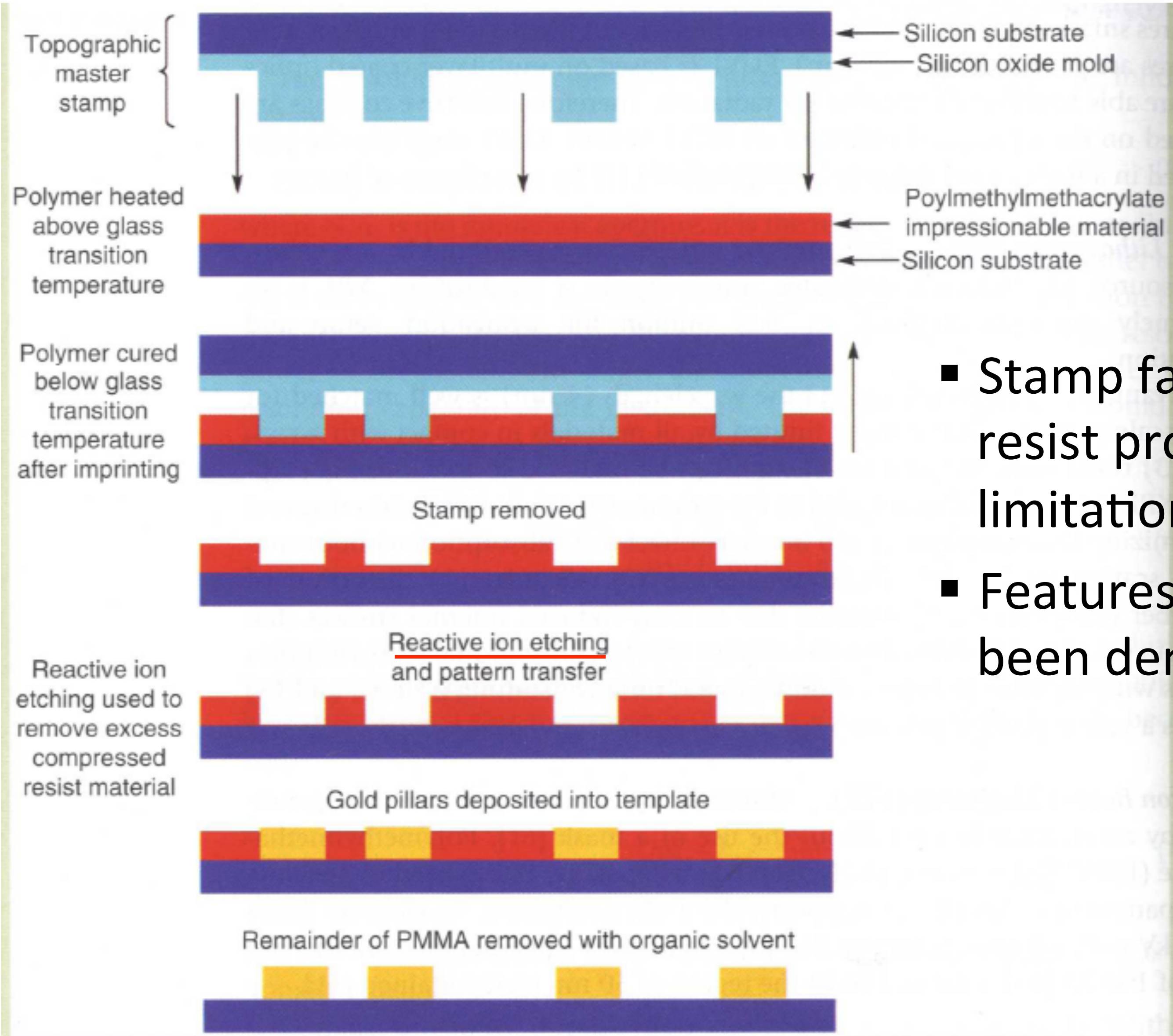


http://www.intel.com



http://www.itrs.net

Nanoimprint lithography



- Stamp fabrication and resist properties/flow are limitations
- Features <5 nm have been demonstrated

Continuous nanoimprint lithography

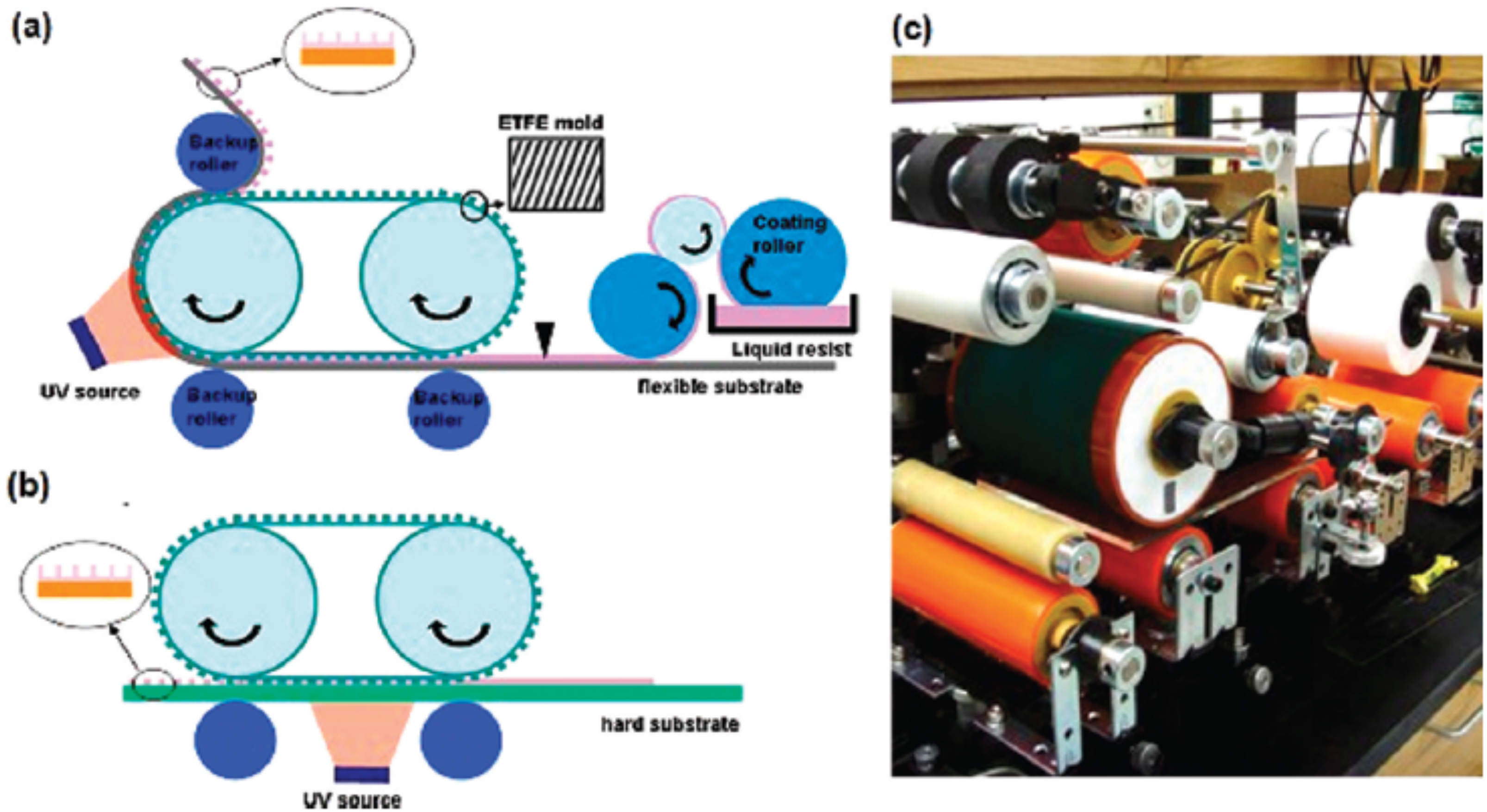


Figure 1. Schematics of (a) R2RNIL and (b) R2PNIL process. (c) Photograph of 6 in.-capable R2R/R2PNIL apparatus.

Ahn and Guo, *ACS Nano* 3(8):2304-2310, 2009.

Continuous nanoimprint lithography

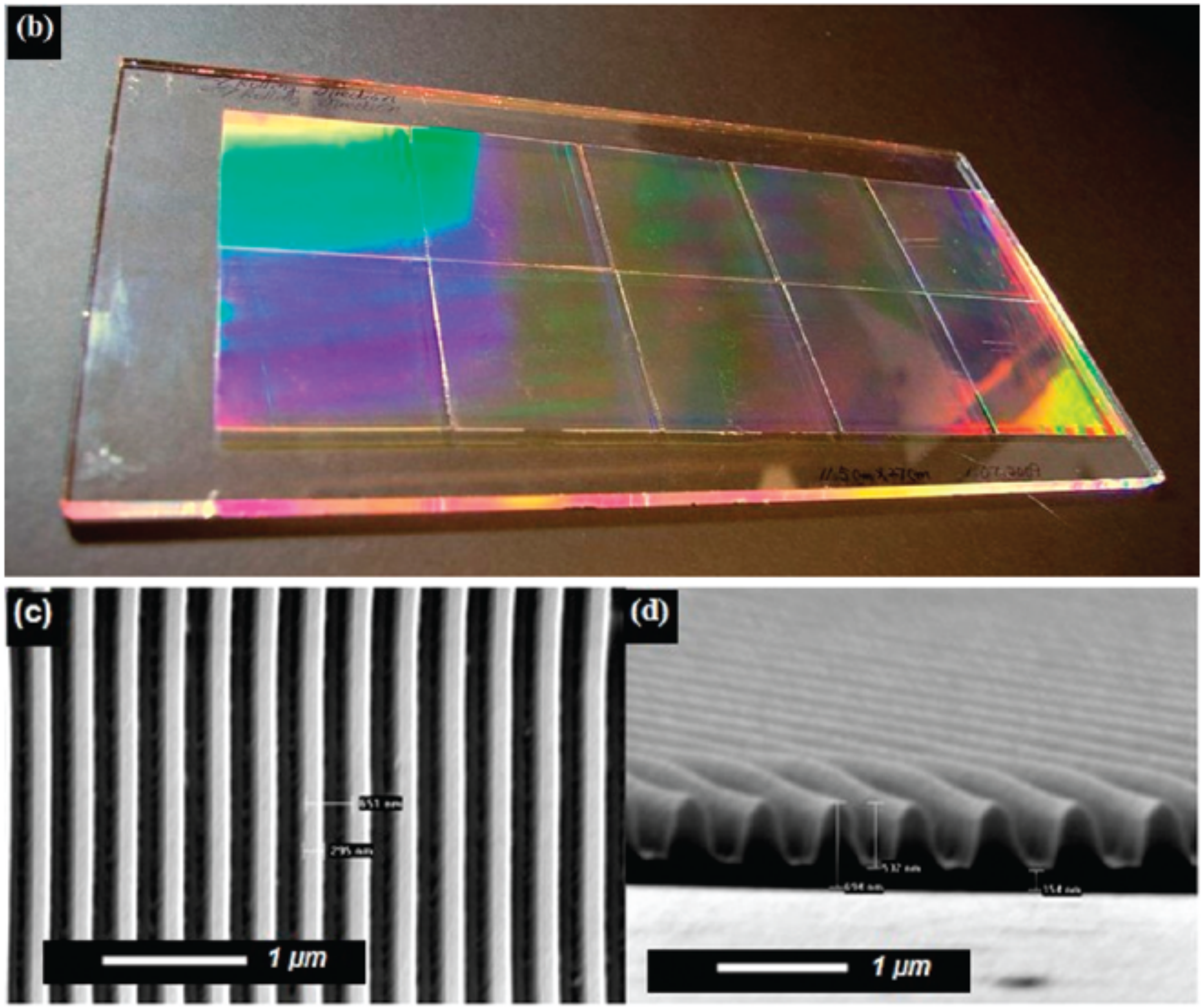
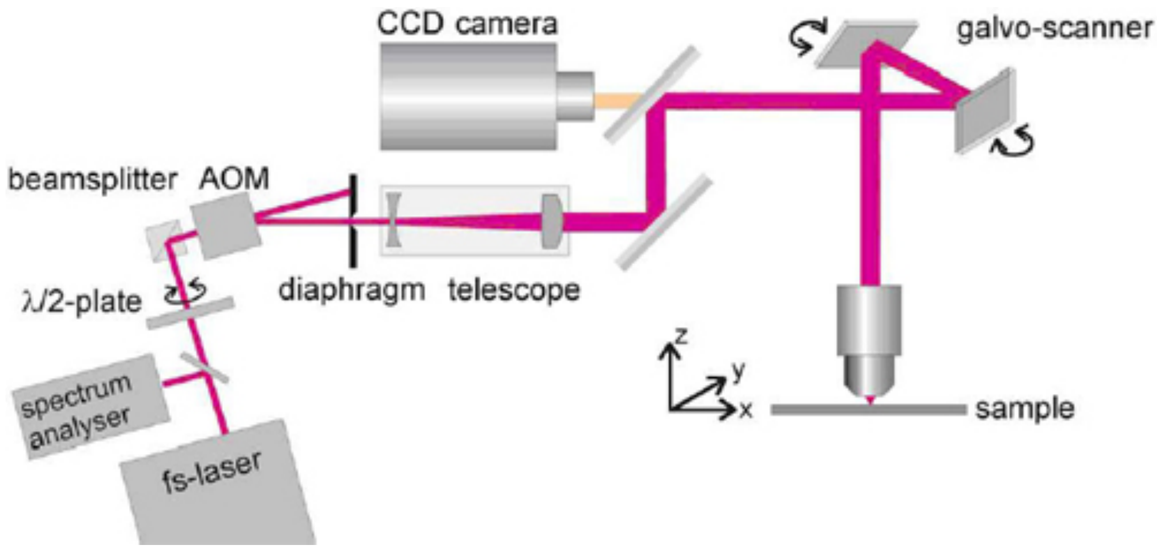


Figure 2. (a) A 4 in. wide, 12 in. long 700 nm period epoxysilicone pattern on flexible PET substrate by R2RNIL process and (b) a 4 in. wide, 10.5 in. long 700 nm period grating pattern on glass substrate. (c,d) SEM images of the patterned grating structure.

Ahn and Guo, *ACS Nano* 3(8):2304-2310, 2009.

Two-photon absorption (TPA)

- Photomodification of a polymer mixture that will be modified upon exposure to **two** photons, not one
- Typically uses fast (~fs) laser pulses
- The nonlinear/threshold nature of this effect enables sub-wavelength resolution
- The laser can be focused into the depth (3D) of a material



Kawata et al., *Nature* 412:697-8, 2001.

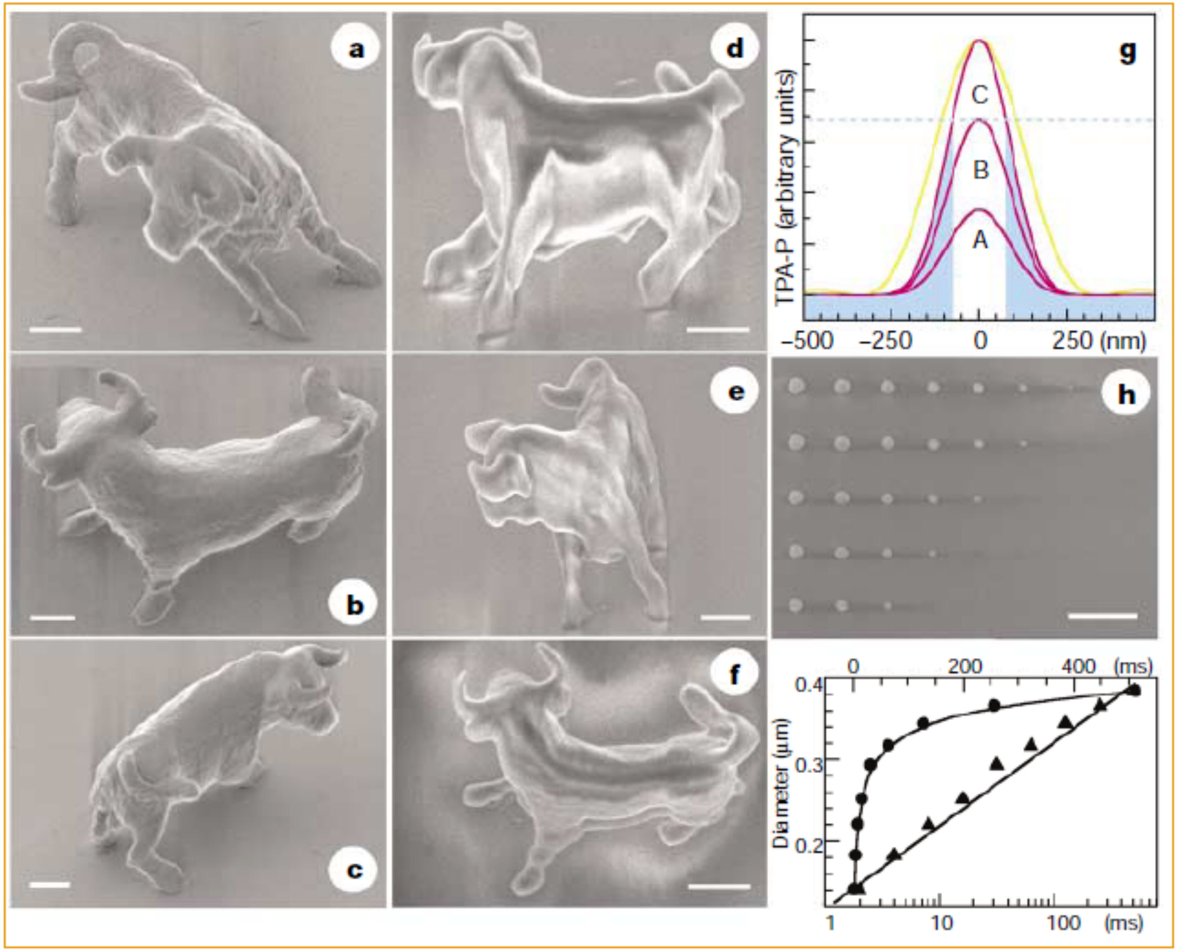
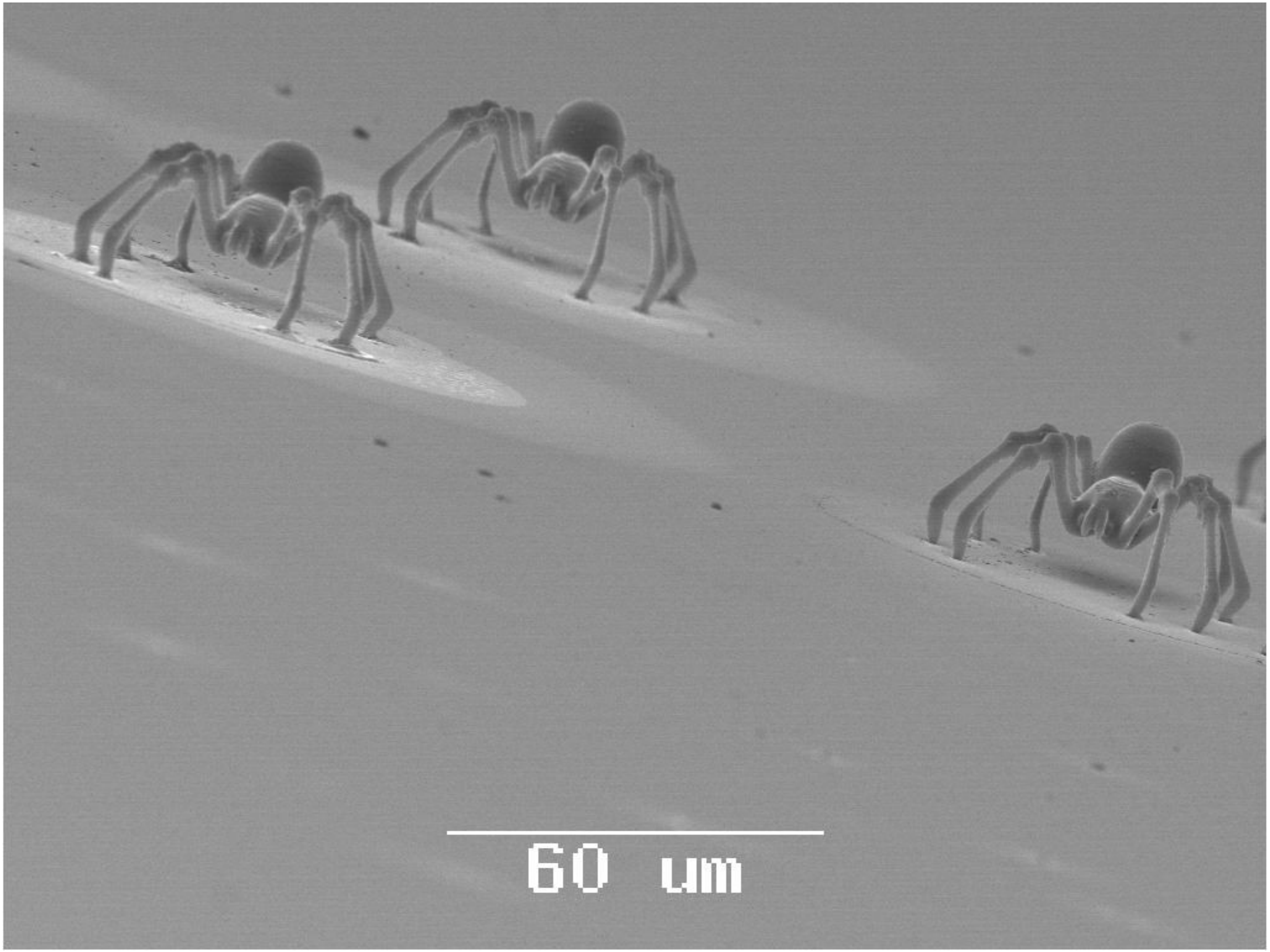


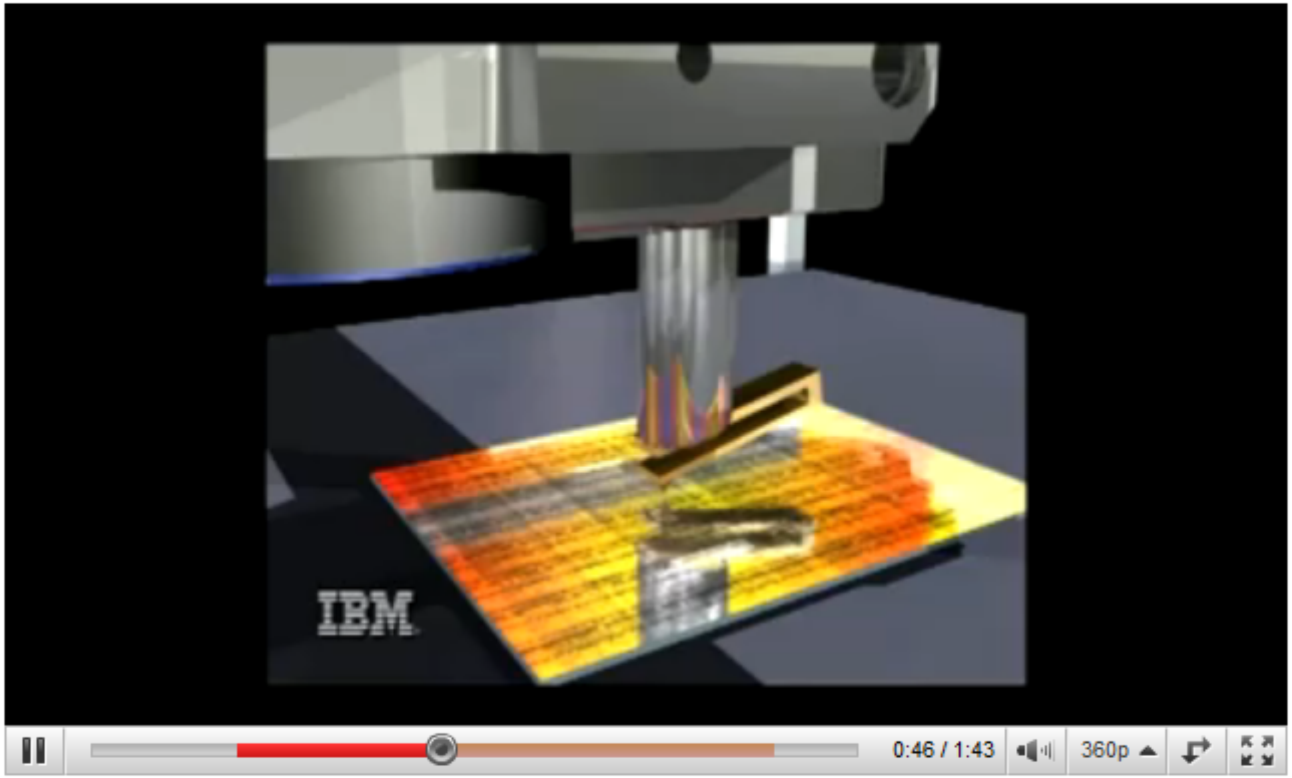
Figure 1 Microfabrication and nanofabrication at subdiffraction-limit resolution. A titanium sapphire laser operating in mode-lock at 76 MHz and 780 nm with a 150-femtosecond pulse width was used as an exposure source. The laser was focused by an objective lens of high numerical aperture (~1.4). **a–c,** Bull sculpture produced by raster scanning; the process took 180 min. **d–f,** The surface of the bull was defined by two-photon absorption (TPA; that is, surface-profile scanning) and was then solidified internally by illumination under a mercury lamp, reducing the TPA-scanning time to 13 min. **g,** Achievement of subdiffraction-limit resolution, where A, B and C respectively denote the laser-pulse energy below, at and above the TPA-polymerization threshold (dashed line). The yellow line represents the range of single-photon absorption. TPA-P, TPA probability. **h,** Scanning electron micrograph of voxels formed at different exposure times and laser-pulse energies. **i,** Dependence of lateral spatial resolution on exposure time. The laser-pulse energy was 137 pJ. The same data are presented using both logarithmic (triangles; bottom axis) and linear (circles; top axis) coordinates, to show the logarithmic dependence and threshold behaviour of TPA photopolymerization. Scale bars, 2 μm.



http://www.laser-zentrum-hannover.de/en/fields_of_work/material_processing/img/nano-spinnen.jpg

Positioning individual atoms

IBM Measures The Force Required To Move Atoms



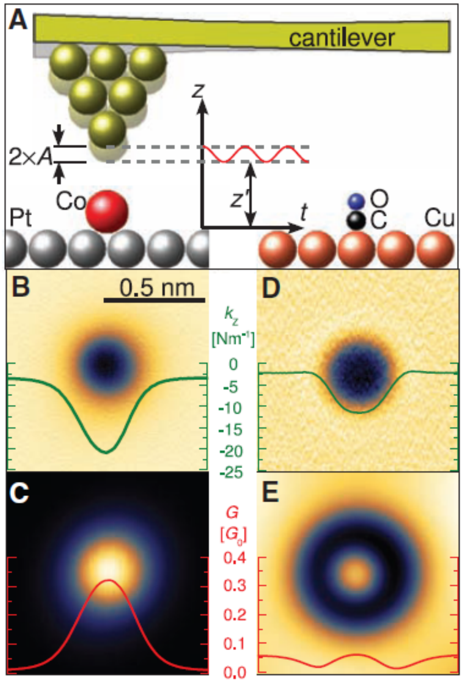
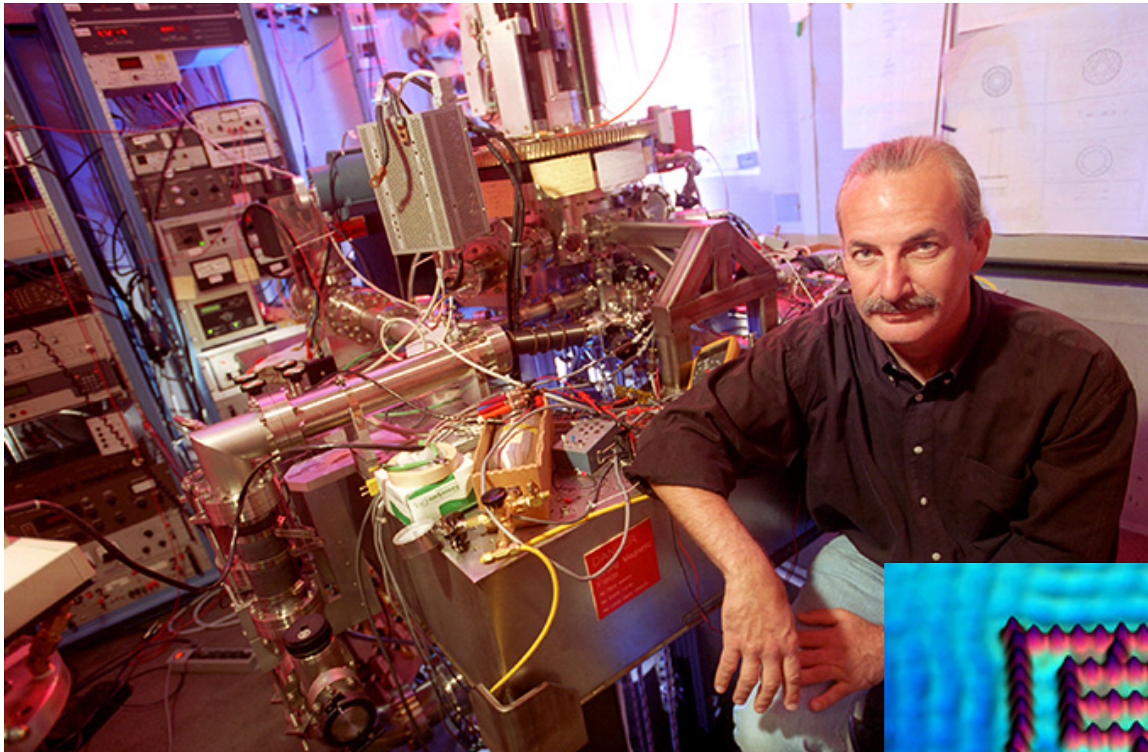
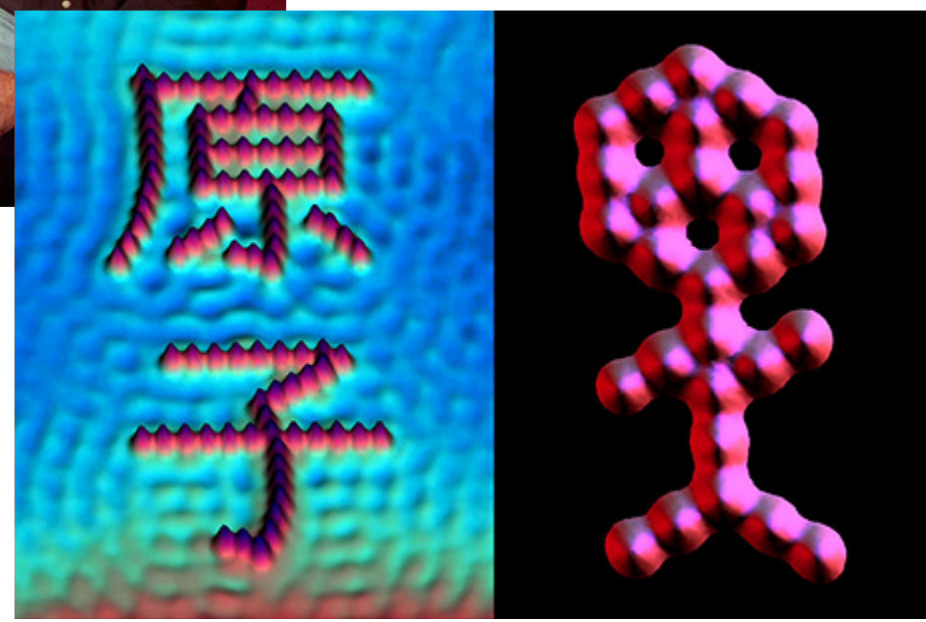


Fig. 1. Simultaneous AFM and STM measurements of individual adsorbates. (**A**) An atomically sharp metal tip is oscillating in z with an amplitude $A = 30$ pm over a flat metal surface on which an individual Co atom or CO molecule is adsorbed. The measured frequency shift of the cantilever from its natural resonance frequency is proportional to the vertical stiffness k_z of the tip-sample interaction. A small bias voltage of 1 mV was applied between tip and sample to measure the tunneling current, which is

http://www.youtube.com/watch?v=BUq2bQkL1zo&feature=player_embedded#
http://www.sciencemag.org/cgi/content/abstract/319/5866/1066

Positioning individual atoms

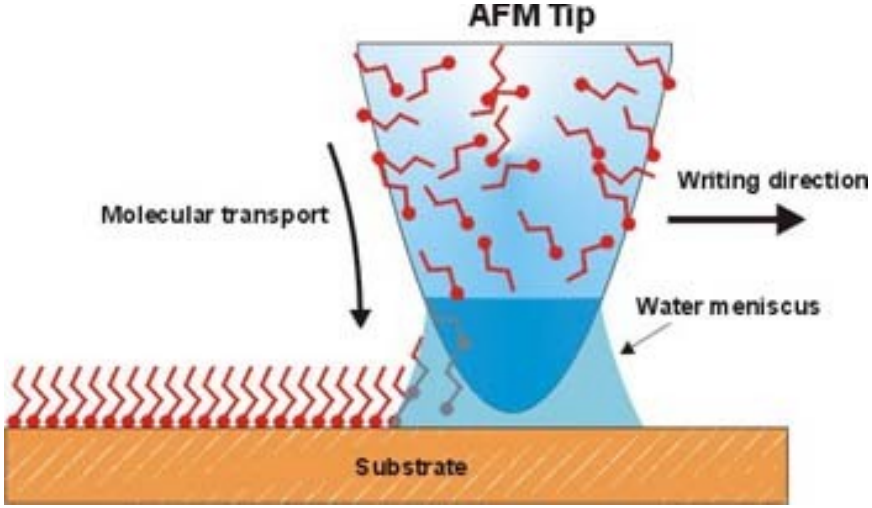


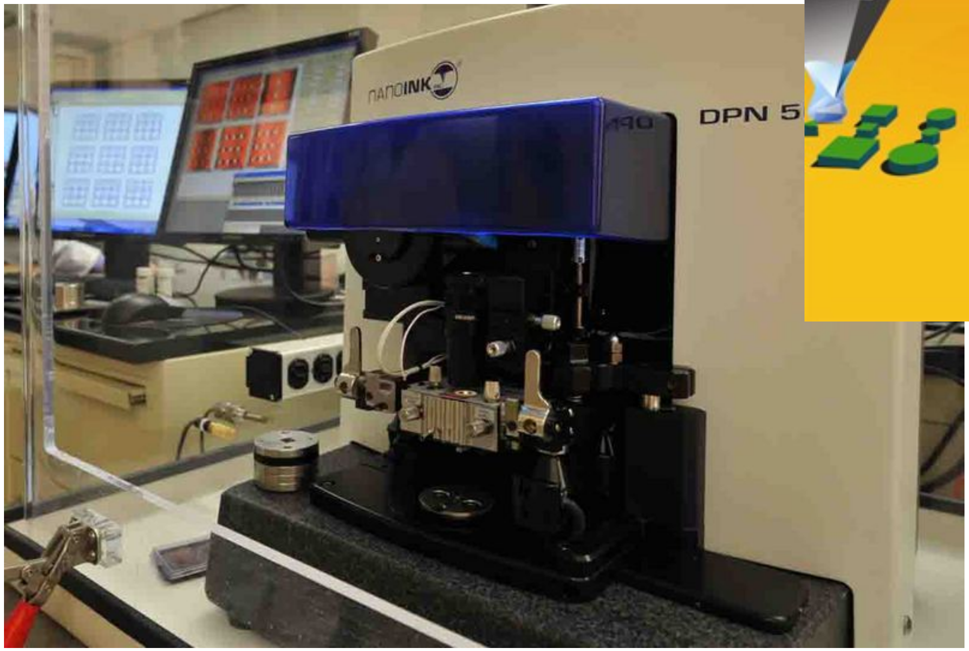


"Atom"

http://www.wired.com/gadgetlab/2009/09/gallery-atomic-science/

Dip-pen nanolithography (DPN)





Mirkin group, Northwestern; Nano-Ink
http://www.nature.com/nnano/journal/v2/n3/full/nnano.2007.39.html

Dip-pen nanolithography (DPN)

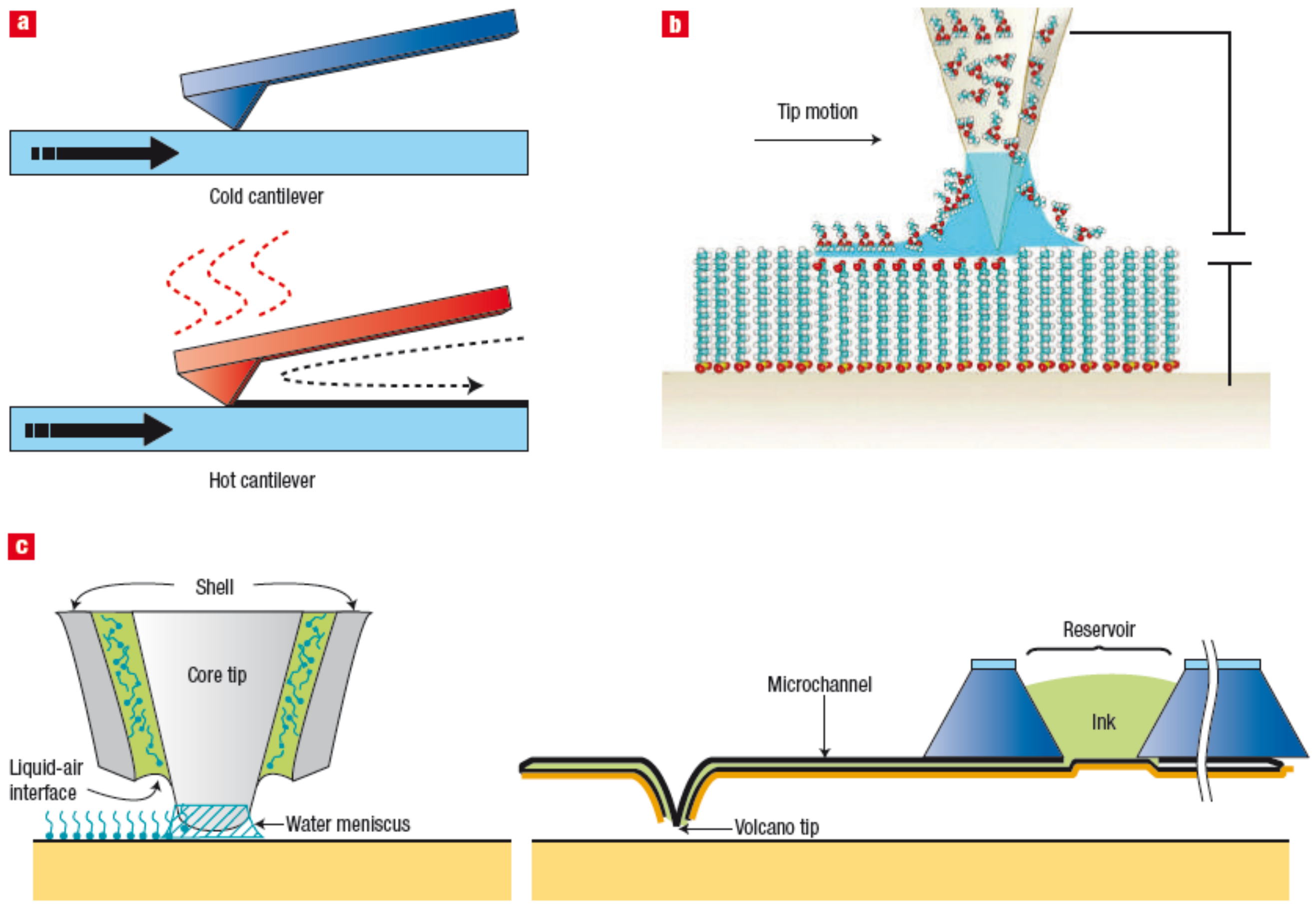


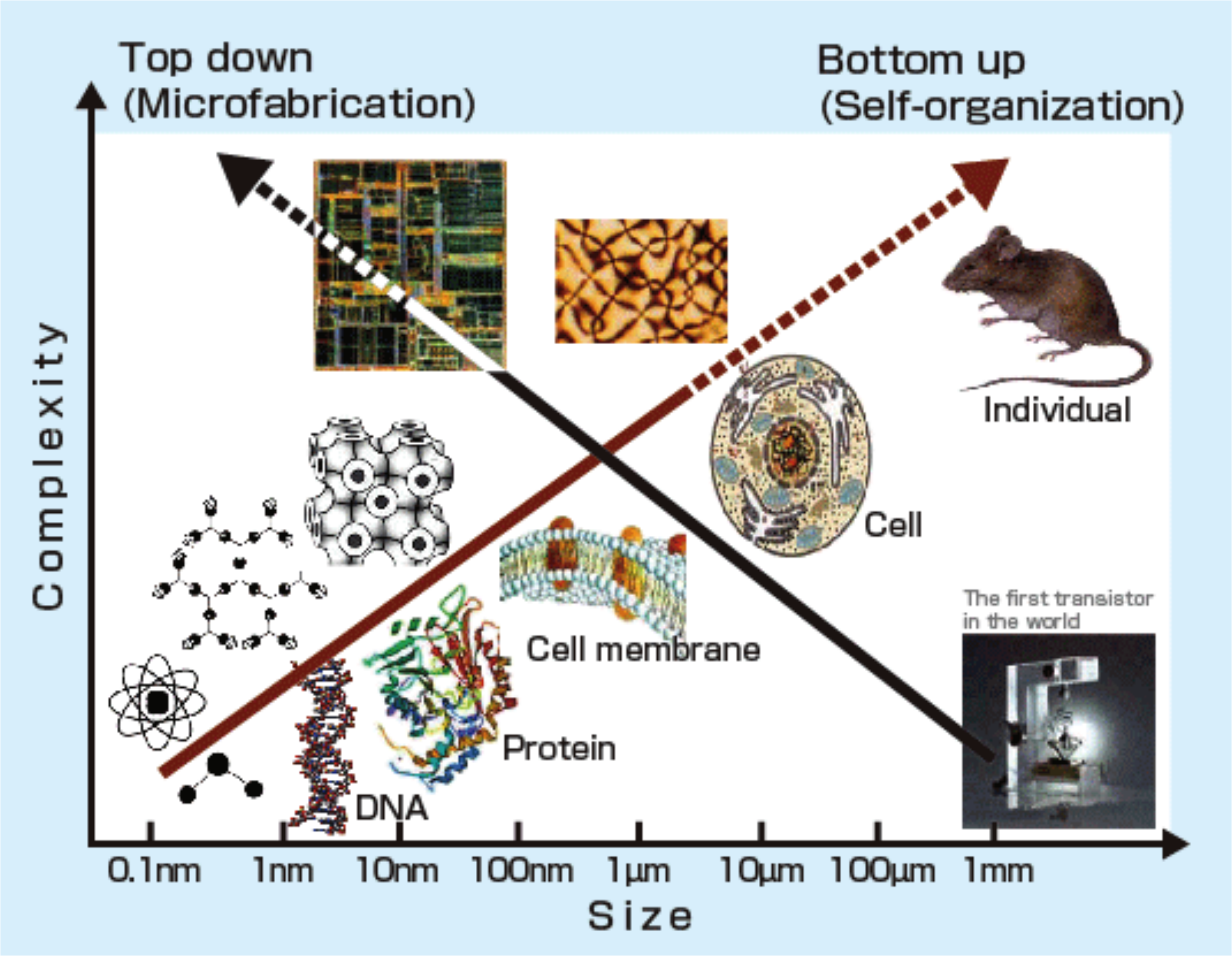
Figure 5 Examples of variants of DPN. **a**, Thermal DPN, which uses a heated AFM cantilever whose tip is coated with a solid 'ink'. When the tip is hot enough, the ink melts and flows onto the substrate. No deposition occurs when the tip is cold, so imaging without any unintended deposition is possible. **b**, Electro pen nanolithography on an octadecyltrichlorosilane (OTS)-coated surface. The terminal methyl group of the OTS is converted to a reactive COOH-terminated surface (OTSox) by applying a voltage between the conducting AFM tip and the conducting silicon substrate in a humid environment. 'Ink' molecules are delivered from the 'inked tip' to the reactive OTSox surface, forming a second layer in the same sweep. No second layer is formed on the methyl-terminated regions. **c**, Writing mechanism of the Nano Fountain Pen. Molecular ink fed from the reservoir forms a liquid–air interface at the annular aperture of the volcano tip. Molecules are transferred by diffusion from the interface to a substrate and a water meniscus is formed by capillary condensation.

http://www.nature.com/nnano/journal/v2/n3/full/nnano.2007.39.html

“Bottom-up” methods

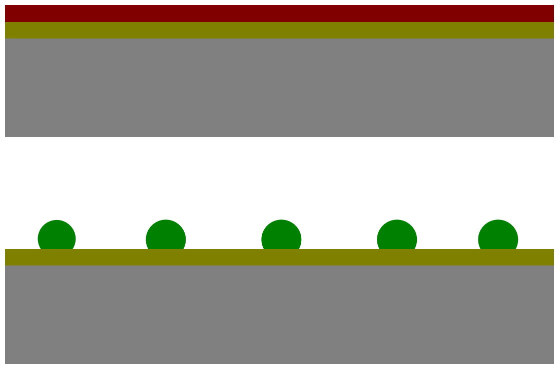
- Begin with atoms and molecules (bottom), which react under chemical or physical circumstances to form nanostructures.
- Examples:
  - Chemical vapor deposition (CVD); atomic layer deposition (ALD)
  - Crystal growth
  - Self-assembly
    - Building blocks
    - Interactions
    - Applied forces
  - Biological methods
- Hybrids…

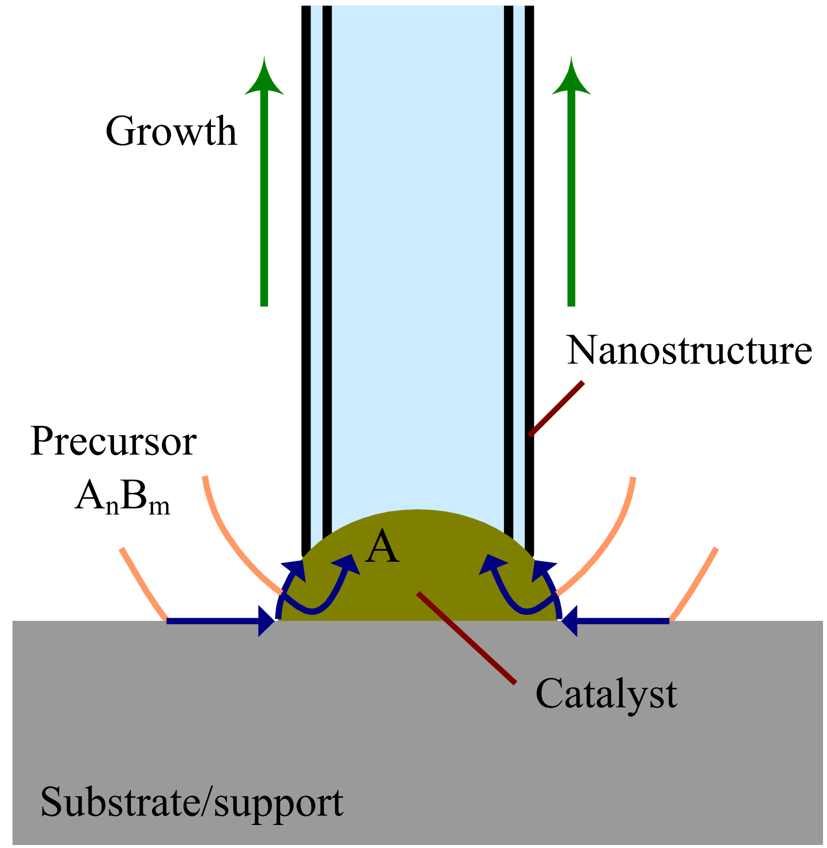
Where is the crossover?



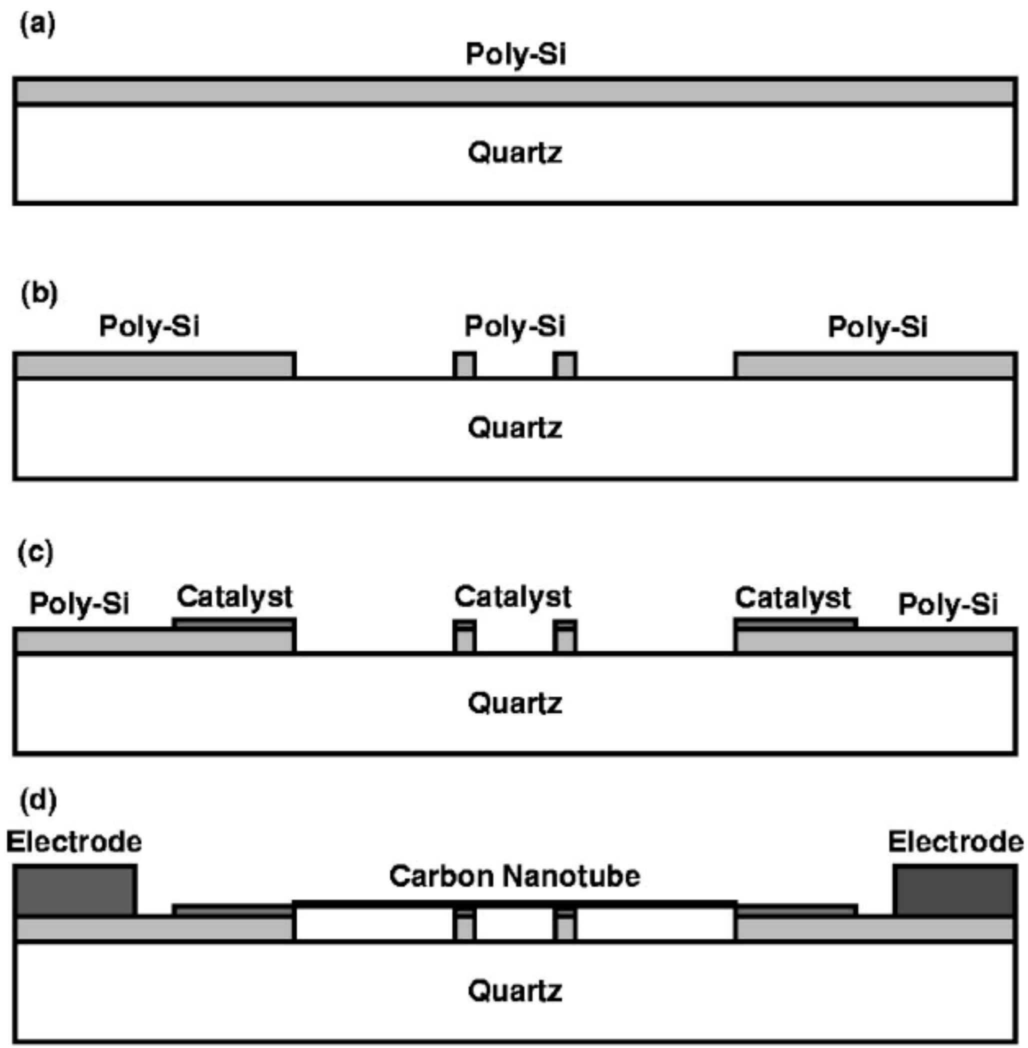
http://www.aist.go.jp/aist_e/aist_today/2007_23/nanotec/nanotec_02.html

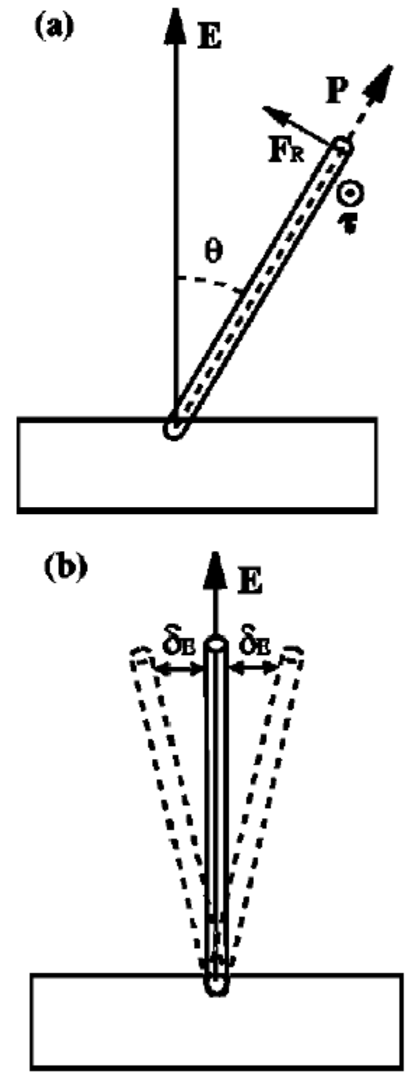
Growth of nanotubes and nanowires





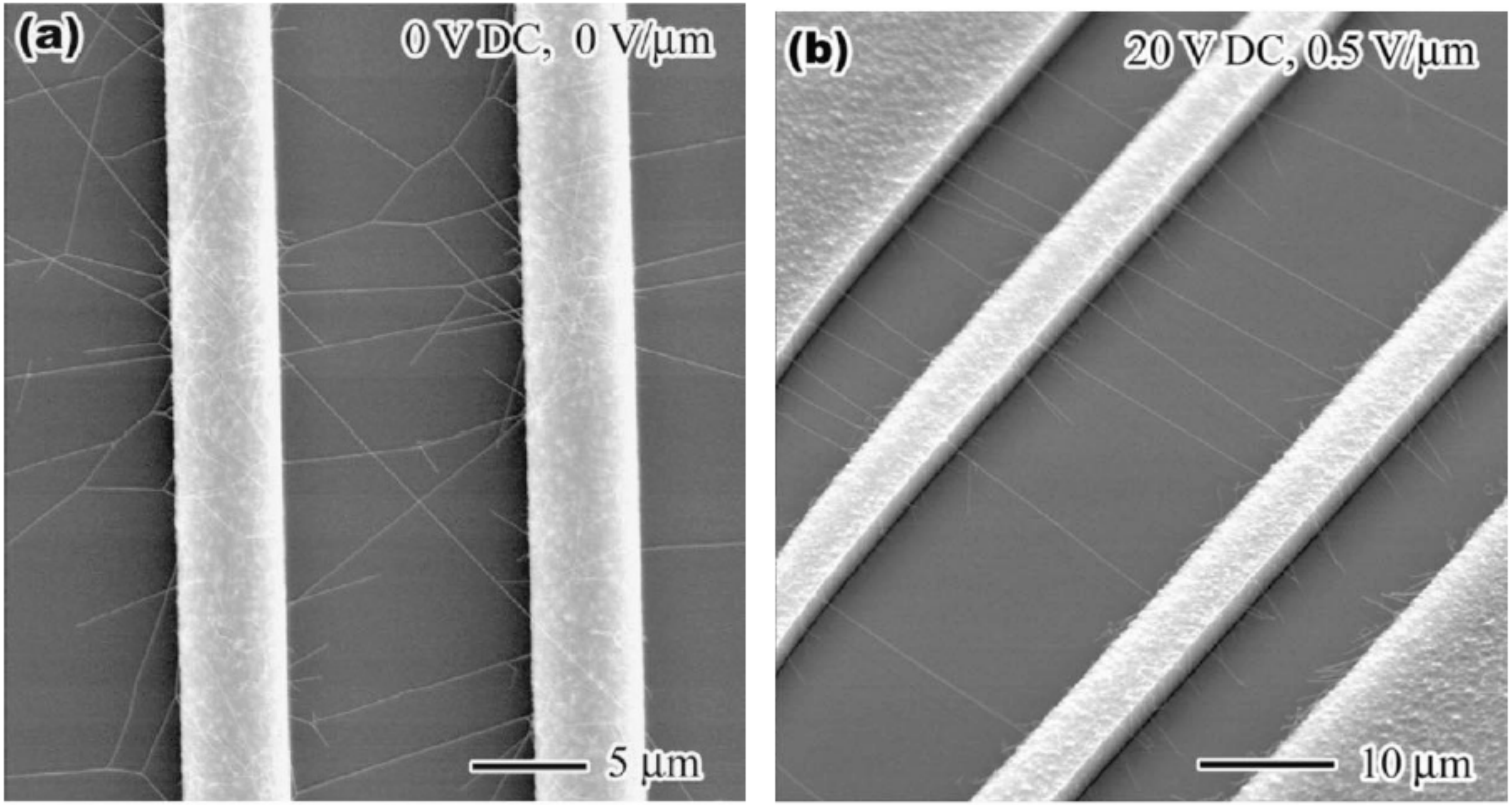
Electric field-directed growth of CNTs

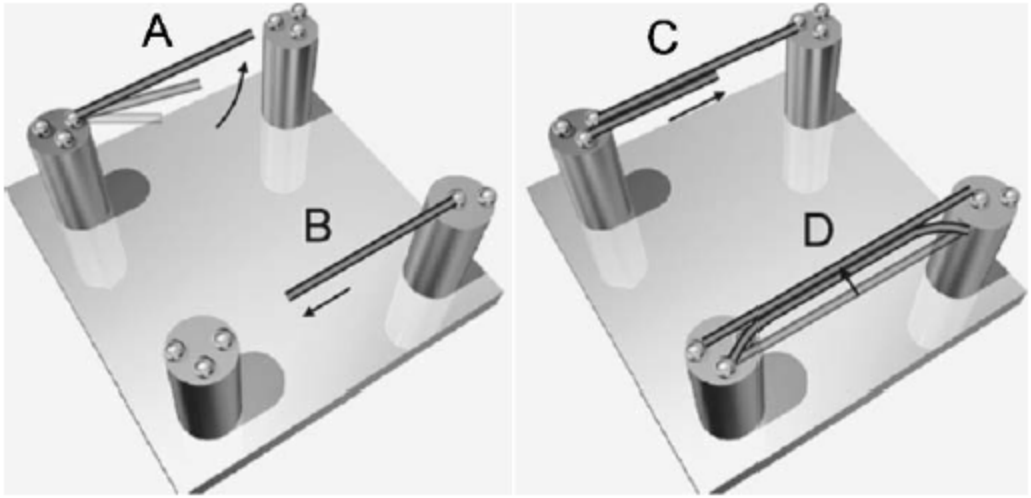




→ Alignment force vs. thermal vibration

Zhang et al., Applied Physics Letters 79, 2001





Zhang et al *Appl Phys Lett* 79, 2001
Homma et al *Appl Phys Lett* 88, 2006

Templated self-assembly

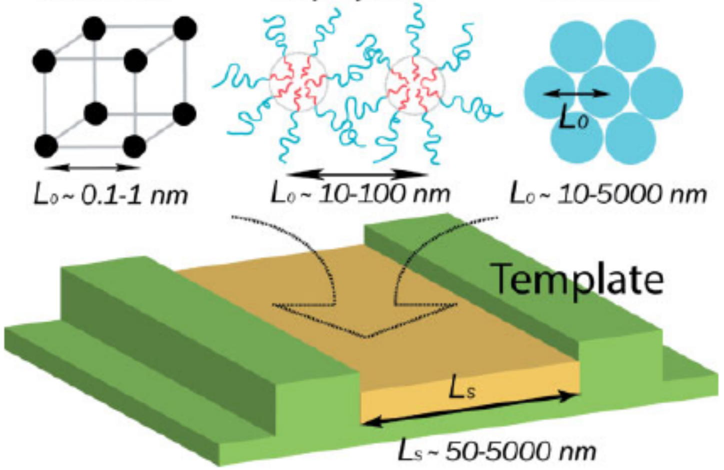


Figure 1. Illustration of some types of TSA systems. Characteristic lengths (L_0) of crystalline materials, block copolymers, and colloid assemblies and the characteristic length (L_S) of the template are indicated.

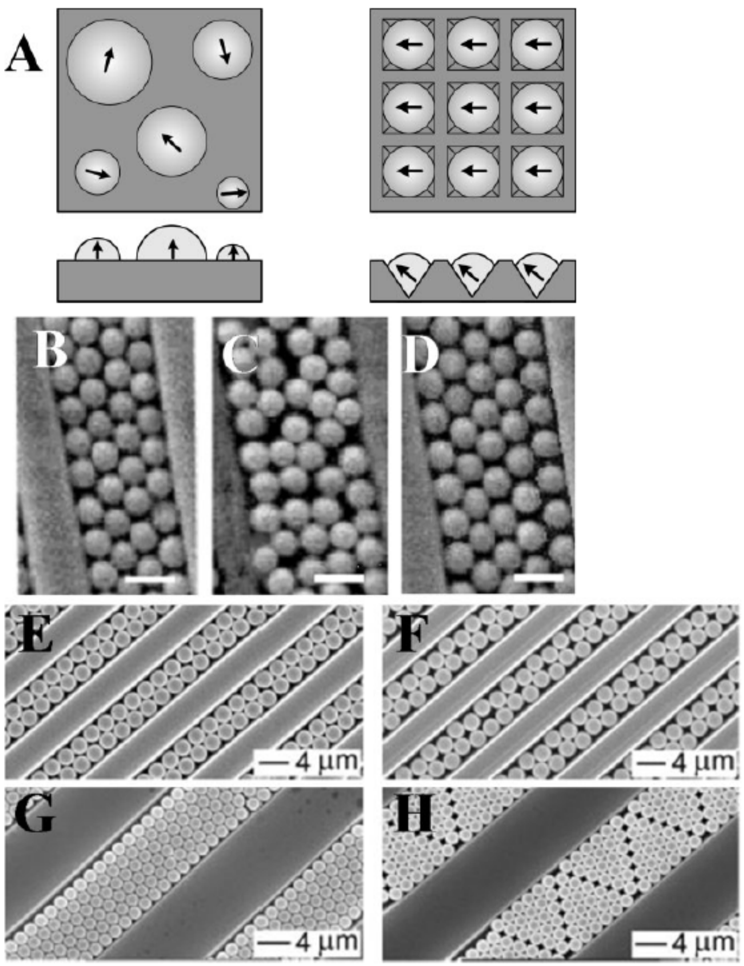
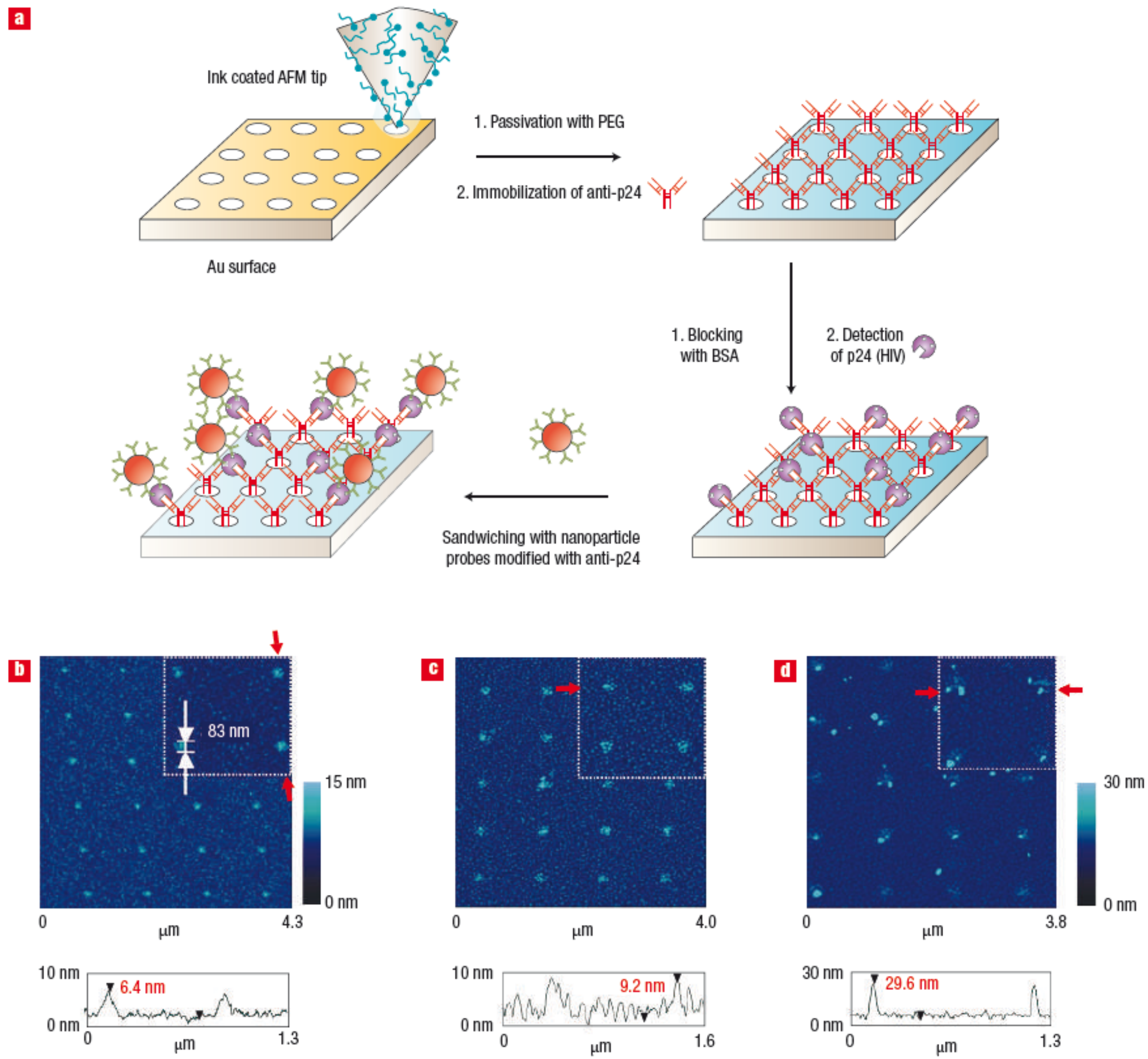


Figure 2. A) Use of topography and dewetting of Au films to create ordered particle arrays [14]. Particles on a flat substrate have random in-plane orientations, while particles on a topologically patterned substrate are crystallographically oriented. The arrows indicate the [111] direction. B–D) Effect of confinement on organization of colloidal particles deposited by an electrophoretic method [17]. The order–disorder–order transition in the colloidal array depends on commensurability of particle diameter and groove width. (Widths of the grooves: B) 2.22 µm, C) 2.51 µm, D) 2.72 µm.) Reprinted from [17]. E–H) Effect of incommensurability on colloidal particles deposited by flow technique [18]. E,F) 2.5 µm polystyrene (PS) bead arrays within channels 5.0 and 5.8 µm in width, respectively. G,H) 1.75 µm PS beads within channels 10.0 and 10.5 µm in width, respectively. Reprinted from [18].

http://doi.wiley.com/10.1002/adma.200502651

Molecular recognition using DPN patterns



http://www.nature.com/nnano/journal/v2/n3/full/nnano.2007.39.html

Placing particles in gaps by electrophoresis

"An alternating current is used to create a gradient of electrical field that attracts particles in between the two leads used to create the potential. Assembly is achieved when dielectrophoretic forces exceed thermal and electrostatic forces; the use of anchoring molecules, present in the gap,improves the final assembly stability."

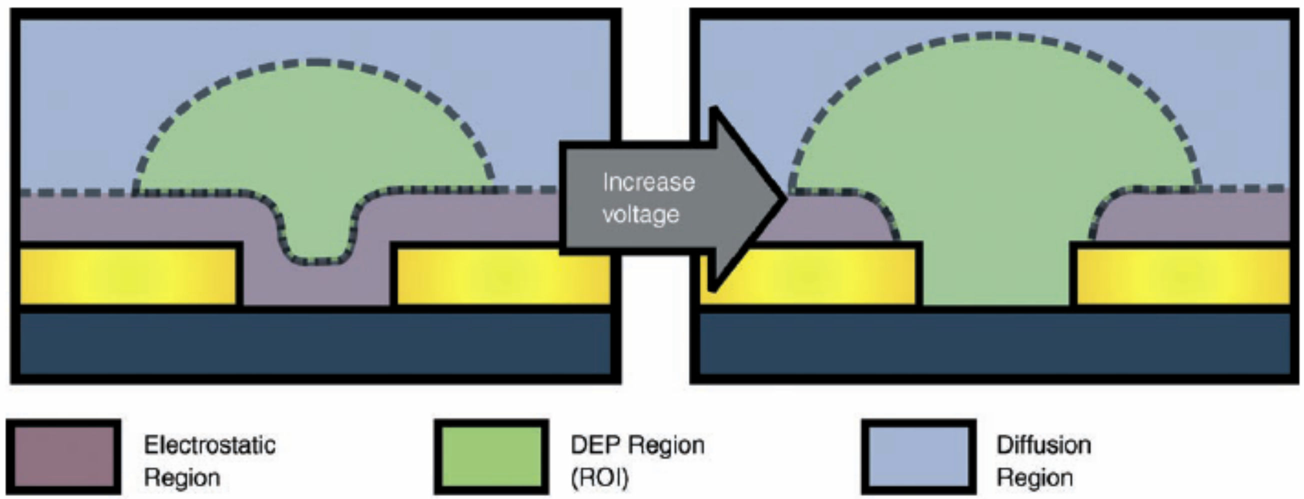


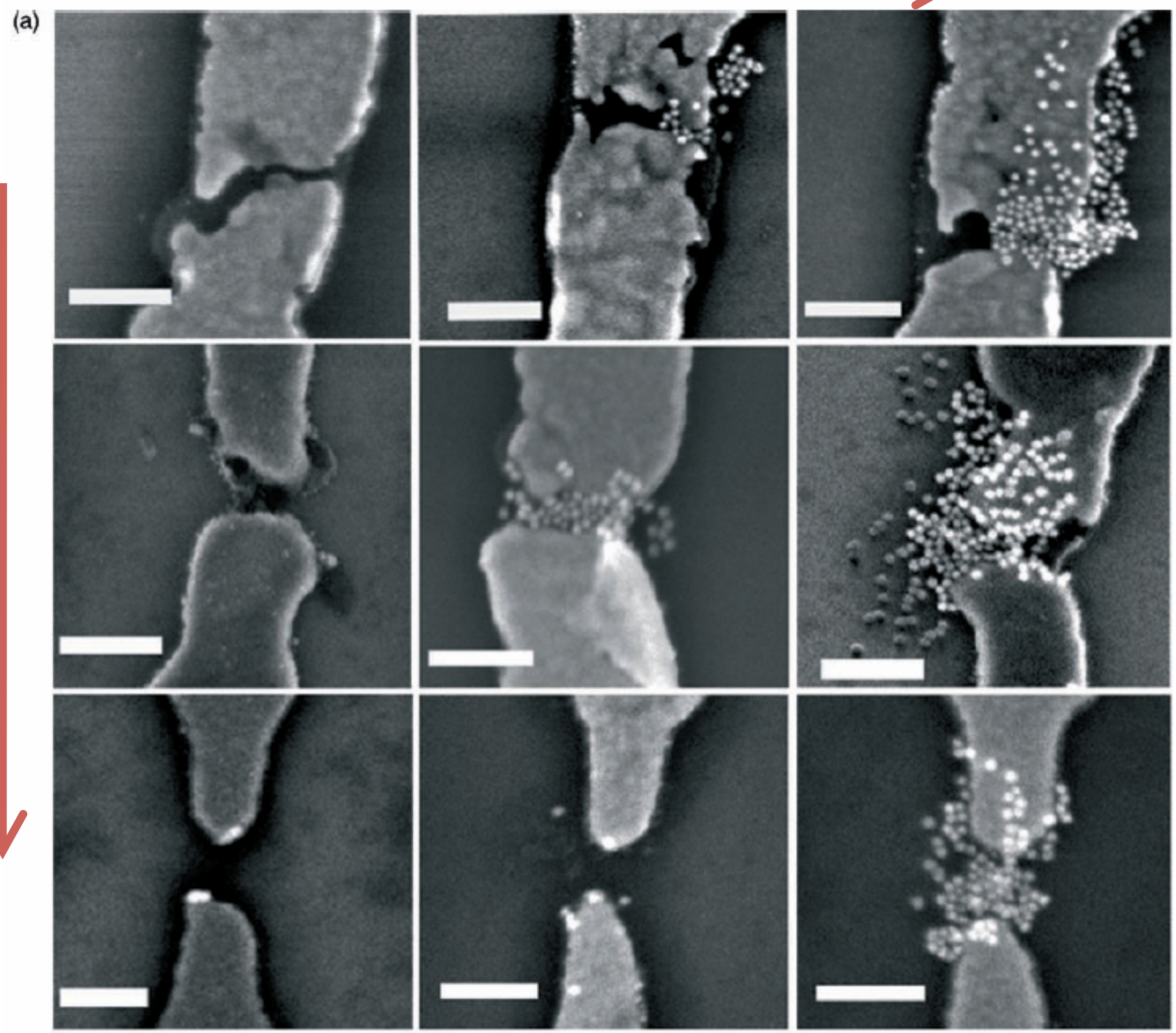
Figure 7. Schematic image showing regions where different forces dominate during DEP assembly of nanoparticles into nanogaps at voltages lower (left) and higher (right) than the threshold voltage.

- Motion is diffusive (Brownian) far from gap
- Substrate-particle repulsion dominates at low voltage
- "DEP region" grows and dominates at high voltage

Barsotti et al., Small 3(3):488, 2007.

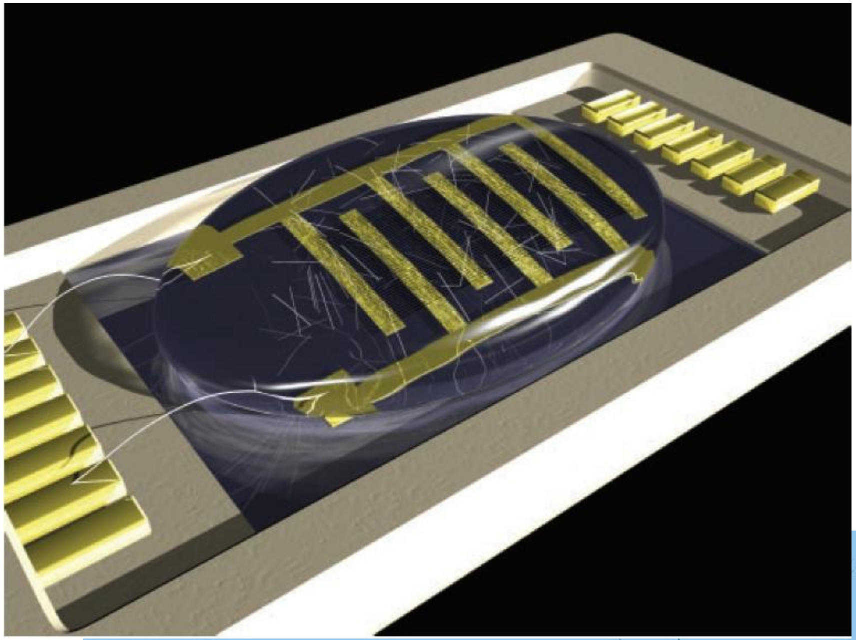
V = 1.5 V → 2V → 3V

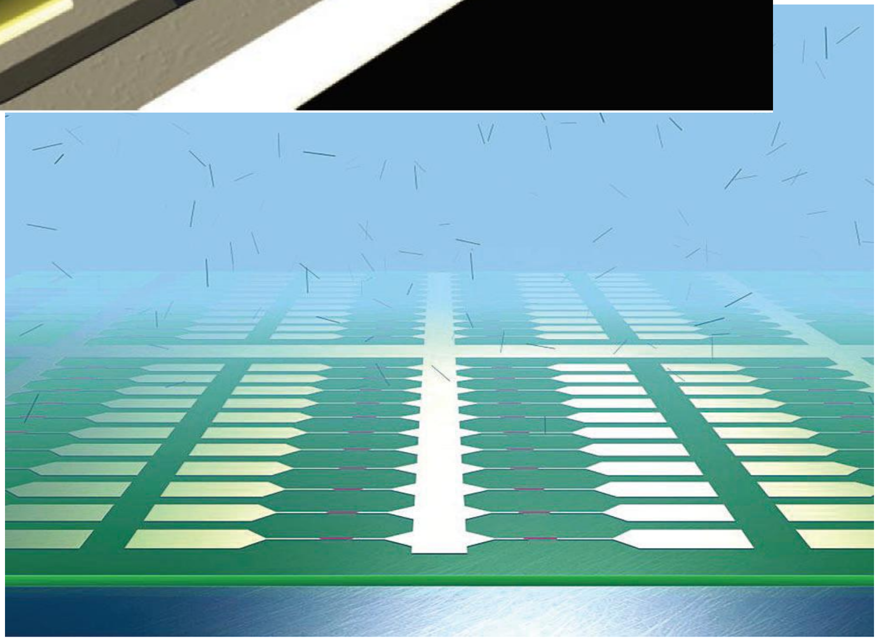
g = 30 nm → 80 nm → 125 nm

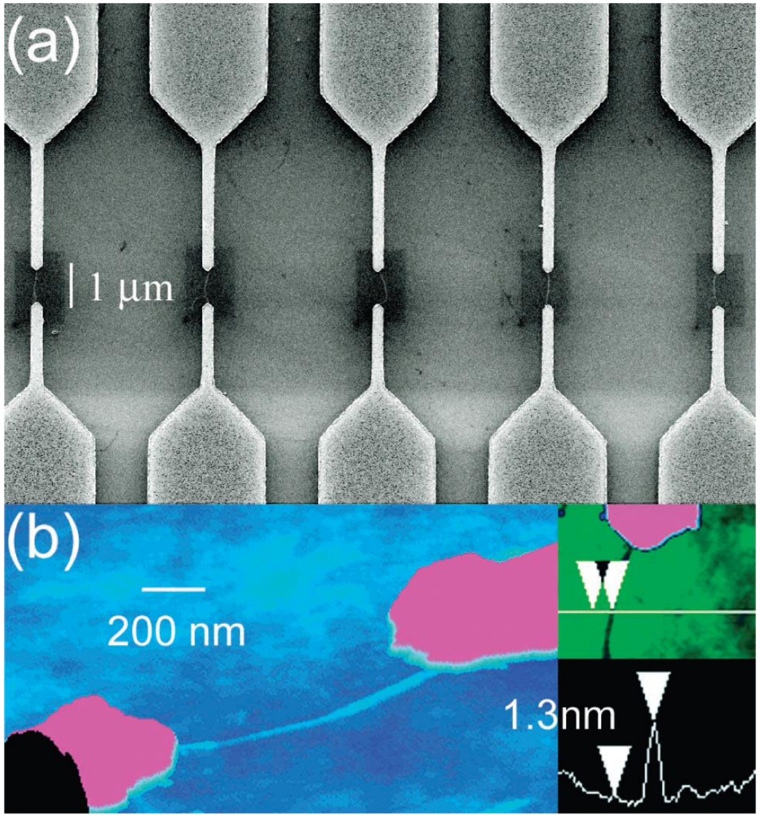


Barsotti et al., Small 3(3):488, 2007.

Dielectrophoresis for positioning CNTs







Vijayaraghavan et al., *Nano Lett*, V.7 No. 6, 1556-1560, 2007.

Some important considerations

- Alignment
- Registry
- Specificity and strength of interactions
- Defect density
- Process compatibility (chemistry, temperature)

Generations of Products and Productive Processes

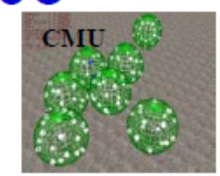
Timeline for beginning of industrial prototyping and nanotechnology commercialization (2000-2020)

1st: Passive nanostructures (1st generation products)
Ex: coatings, nanoparticles, nanostructured metals, polymers, ceramics

~ 2000

2nd: Active nanostructures Ex: 3D transistors, amplifiers, targeted drugs, actuators, adaptive structures

~ 2005



3rd: Systems of nanosystems
Ex: guided assembling; 3D networking and new hierarchical architectures, robotics, evolutionary

~ 2010

4th: Molecular nanosystems
Ex: molecular devices 'by design', atomic design, emerging functions

~ 2015-2020

Converging technologies
Ex: nano-bio-info from nanoscale, cognitive technologies; large complex systems from nanoscale

Increased Complexity, Dynamics, Transdisciplinarity

Slide by M. Roco

Reference: AIChE Journal, Vol. 50 (5), 2004